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The legacy of historic mining and water
quality in a heavily mined
Scottish river catchment

Simon Haunch



College of Science and Engineering at the University of Edinburgh
Doctor of Philosophy

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Declaration

This thesis represents the culmination of four years of work. The work presented is my own; where content has been published or submitted for publication elsewhere, I have noted this accordingly. This thesis has not been submitted for any other professional qualification.

Simon Haunch

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I would like to start by thanking my supervisors Alan MacDonald and Christopher McDermott for offering me the opportunity to undertake this project and for their encouragement and support over the last four years. I would also like to thank Neil Brown for providing me with advice and data in addition to financial support to undertake site investigation works. I'm indebted to Barbara Palumbo-Roe for her advice and assistance in covering the cost of analysis on the majority of my mine water samples. I'm equally indebted to Nick Odling for assistance and support in getting to grips with XRD analysis and interpretation. I would like to thank Helen at the BGS for allowing me to intermittently invade her office over the last few years.

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Abstract

Mine abandonment and the discharge of contaminated mine water is recognised globally as a major source of surface water and groundwater pollution. Contamination generally arises from the oxidation of sulphide minerals, principally pyrite, by the mining process, and the subsequent chemical reactions can lead to the discharge of mineralised, often acidic, iron, and sulphate rich waters. In many historically mined river catchments, mine water discharge is the main cause of poor water quality. Within the UK, managing the legacy of abandoned mines is one of the principal challenges presented by modern environmental legislation, particularly the EU Water Framework Directive, a challenge that is exacerbated by the diverse and widespread nature of historical mining.

The impact and hazard associated with abandoned mining in one of the UK's most intensively mined regions, the Almond River Catchment, Scotland, was examined via: 1) a detailed GIS mapping and investigation of historical mining processes in the catchment, 2) mine site discharge sampling, 3) detailed site investigations, 4) geochemical modelling of four mine waste sites and 5) analysis of temporal and spatial river water quality in the catchment. The results are then brought together to produce a catchment scale mine water hazard map.

Mapping has identified over 300 mine sites in the catchment including coal, oil shale and ironstone mine wastes and flooded coal and oil shale mines. The historical development of oil shale retort methods has been shown to have an impact on potential hazard.

Sampling of discharge waters from the different mining activities, in conjunction with detailed mineralogical analysis and geochemical modelling at the four mine waste sites has characterised the main hazards. *Ironstone* and pyrite bearing *coal mine wastes* discharge waters with highly elevated Fe and sulphate concentrations, up to 160mg l^{-1} and 1900mg l^{-1} respectively, due to extensive pyrite oxidation and acid generating salt dissolution (principally jarosite). *Coal mine wastes* show variable mineralogy, due to the diverse nature of coal bearing strata, and discharge waters with variable chemistry. *Oil Shale mine wastes* are generally depleted in pyrite due to historic processing and discharge low sulphate waters with moderately elevated Fe concentrations, up to 5mg l^{-1} . *Flooded coal mines* discharge sulphate dominant alkaline waters, due to the availability of carbonate minerals in the mine complex, with elevated Fe concentrations, up to 50mg l^{-1} , while *flooded oil shale mines* discharge waters with moderately elevated Fe concentrations, up to 4mg l^{-1} , due to lower pyrite content in mine strata and reduced availability of oxygen related to mine abandonment age.

Once in the surface water environment iron and sulphate display significant concentration-flow dependence: iron increases at high flows due to the re-suspension of river bed iron precipitates ($\text{Fe}(\text{OH})_3$); sulphate concentrations decrease with increased flow as a result of dilution. Further examination of iron and sulphate loading at low flows indicates a close correlation of iron and sulphate with mined areas; cumulative low flow load calculations indicate that coal and oil shale mining regions contribute 0.21 and 0.31 g/s of iron, respectively, to the main Almond tributary. Decreases in iron loading on river sections demonstrate the deposition and diffuse storage of iron within the river channel. This river bed iron is re-suspended with increased flow resulting in significant transport of diffuse iron downstream with load values of up to 50 g/s iron.

Based on this hazard classification, a catchment scale mine water hazard map has been developed. The map allows the prioritisation of actions for future mine water management.

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Copy of the Applied Geochemistry Paper:

Haunch et al, in press; Flow dependent water quality impacts of historic coal and oil shale mining in the Almond River catchment, Scotland.

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Chapter 1

Mine water: a catchment scale approach

1.1 Introduction and objectives

Discharge of contaminated mine waters from abandoned mines is a global threat to water quality. The global mining industries are growing rapidly due to increasing demand for energy and mineral resources; in 2011, 7678 million tonnes of coal was mined globally, an increase of 6.6% on the previous year (World Coal Association 2012). Historically, the UK exploited significant coal reserves; however, widespread abandonment occurred in the second half of the 20th century and only limited surface coal mining is now undertaken. The largest global producers of coal today are China, USA, India and Australia. In continental Europe, coal mining is still a significant industry, Germany and Poland mined 189 and 139 million tonnes, respectively, in 2011 (World Coal Association 2012).

Mining requires the lowering of groundwater levels to access subsurface mineral resources and the removal of rock overburden, which is of no economic value, to be discarded at surface as mine waste. These actions can result in the oxidation of reduced sulphide minerals, in the mined rocks, releasing metals and other contaminants into groundwater, following mine abandonment. Discharge of these waters into surrounding surface water and groundwater has deleterious impacts on ecology, water quality (Jarvis and Younger 1997) and in some cases, human health if the most eco-toxic metals are released (e.g. Malm et al. 1990, Duker et al. 2005).

The UK, having a long history of intensive mining, provides an excellent place to study the potential long term consequences of mine abandonment on the water environment. Understanding these consequences will hopefully allow the prioritisation of actions to minimise potential future impacts, associated with

abandonment, in the UK and in those countries where mining is currently being undertaken.

The prevalence of historic mining in the UK means mine water discharge accounts for the single largest source of metals such as iron, zinc and copper in UK Rivers (Johnston et al 2008). Historically the impact of mining industries on water quality was tolerated and prior to 1999 the mine operator was not considered legally responsible for the consequences of discharge '*if he is merely 'permitting' a discharge from an abandoned mine*' (Section 89(3) Water Resources Act 1991). The Mines (notice of Abandonment) Regulations 1998, which made the mine operator responsible for environmental impacts, came into force at the end of the 20th century (31.12.1999); however, any mine abandoned prior to this date effectively became the responsibility of the Environment Agency, Scottish Environment Protection Agency and the Coal Authority (Amezaga & Younger 2004). Modern environmental regulation, particularly the EU Water Framework Directive, requires that pollution to the water environment is prevented and where possible the impacts reversed.

Since 1994 the Coal Authority have devised and established 54 mine water treatment schemes across the UK, which prevent the annual discharge of 2500 tonnes of iron and improve water quality in ~200km of UK Rivers, however, this is only a fraction of the ~ 2200 km of river impacted by abandoned coal mines in the UK (Johnston et al. 2008). Furthermore, impacts on water quality are also commonly associated with abandoned non-coal mines such as oil shale, ironstone and metal (e.g. Nuttal and Younger 1999). Therefore, there is a growing demand to manage mine water discharges on a river catchment scale in line with other water quality pressures (e.g. Kimball et al. 1999, Potter et al. 2004, Johnston et al. 2008).

This thesis considers mine water contamination, water quality impact and potential hazard in one of the most heavily mined river catchments in the UK. The primary aim of this research is to '**Assess the mine water hazard and potential cumulative water quality impacts associated with abandoned mines in the Almond River Catchment**'. A variety of mineral resources including coal, oil shale and ironstone

were mined in the Almond Catchment. Oil shale is not well studied compared to more conventional mining such as coal; therefore, the achievement of the primary research aim will require an assessment of the environmental legacy of the oil shale industry. Oil shale was mined to extract a form of oil in the Scottish Shale Oil Industry which was effectively the world first source of ‘unconventional hydrocarbons’. This body of research is the first to specifically consider the legacy of water quality impacts associated with the Scottish Oil Shale Industry.

Modern day exploitation of the remaining Scottish Oil Shale reserves in addition to other shale reserves, in Scotland, and the UK, is receiving increased interest in the commercial and academic sectors (e.g. DECC 2011). Concerns about the potential impacts of shale exploration have been raised within the scientific community, by the media and members of parliament as well as by environmentalist groups. The historic Scottish Oil Shale Industry, although fundamentally different in the mode of exploitation compared to modern unconventional hydrocarbon exploration, offers a ‘worked example’ of enduring pollution from oil shale workings. Therefore, aspects of this body of research will offer insight to exploration and environmental geologists concerned with modern day unconventional hydrocarbon exploration, as well as those concerned with managing the impacts of historic exploitation.

There are a number of objectives to be met to achieve the primary research aim;

1. Define the scale and distribution of historic mining in the catchment
2. Historically review and define the potential environmental consequences of the Scottish Oil Shale Industry
3. Define the relative impact of coal and oil shale mining on water quality in the catchment.
4. Assess the variable nature of mine waste associated with the main historic mine industries in the catchment.
5. Compare and characterise mine water chemistry and hazard associated with the range of abandoned mines sites

6. Develop a hazard map for the catchment to better inform future actions and environmental management.

The objectives of this research require a multifaceted research approach which includes fieldwork, lab work, computer modelling and historical review. Table 1.1 outlines each of the approaches used within this thesis to achieve the objectives listed above. The research, as a catchment study, is unlikely to be exhaustive in each of the aspects of research but will use them collectively to provide a detailed overview of the issues within this and other historically heavily mined river catchments. This work will provide a foundation for further study into more detailed aspects of mine water in Central Scotland, and will hopefully act as a bench mark for similar catchment approaches to mine water contamination worldwide.

	GIS analysis	Acquire and Interpret data from external sources (SEPA, CA, WLC)	Historical Review	Reconnaissance Field Work	Sampling and Water Analysis	Detailed Site Investigation inc. small drilling rig	XRD Analysis	Geochemical Modelling
1. Mining Scale and Distribution	✓	✓	✓	✓				
2. Oil Shale Industry	✓	✓	✓	✓				
3. Water Quality Impact	✓	✓						
4. Mine Waste			✓	✓	✓	✓	✓	✓
5. Mine Water				✓	✓			✓
6. Hazard Map	✓				✓			

Table 1.1- Outlines the main objectives (left) of the study and approaches and techniques (top) used within each of the thesis chapters to achieve these aims

1.2 The Almond Catchment

The Almond River Catchment is part of the larger Forth Basin in the Central Belt of Scotland. The river discharges into the Firth of Forth at Cramond, close to Edinburgh, and drains an area of approximately 370 km². The source of the Almond River is several kilometres north of the town of Shotts in North Lanarkshire and from here the river runs NE across the county of West Lothian passing the towns of Harthill, Whitburn, Livingston, Fauldhouse, West Calder and Broxburn, as well as the M8 and M9 motorways (Figure 1.1). The landscape in the catchment is a mix of post industrial, agricultural and urban related to historic mining industries and urban development due to rapid influx of mine workers in the 19th century.

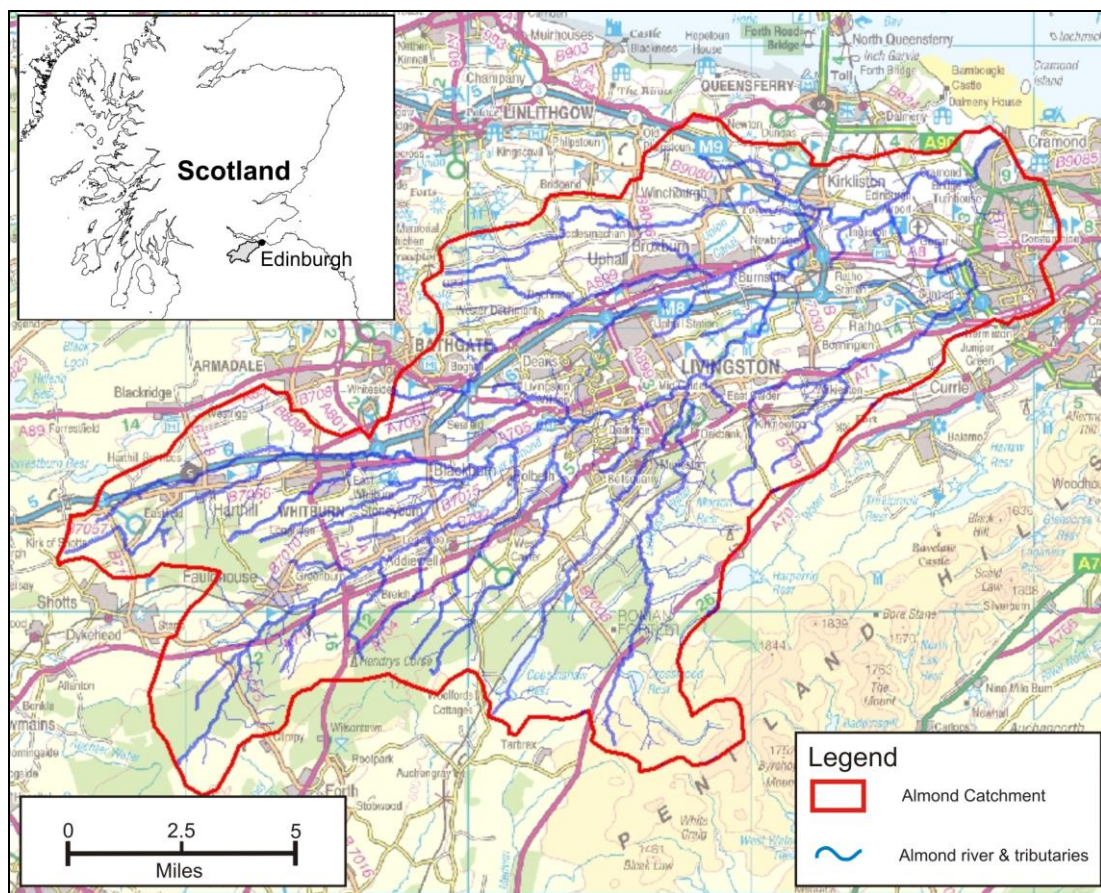


Figure 1.1- The Almond River Catchment with the main river and tributaries in blue and watershed boundary in red. The main settlement areas of Whitburn, Bathgate and Livingston are shown; to the east the catchment incorporates the eastern west edge of the suburbs of the Scottish Capital- Edinburgh. The River Almond discharges into the Firth of Forth at Cramond shown at the top of the map. Contains Ordnance Survey data © Crown Copyright and database rights 2012

The geology of the catchment is dominated by Carboniferous aged marine-deltaic sediments containing significant mineral resources. Early mining in the region dates back to the 12th century when monks mined coal; some limited metal mining in the Bathgate Hills was undertaken in the early 17th century (Cadell 1925), however, it wasn't until the 1840s that coal mining was undertaken on a significant industrial scale (Hassan 1976, Hutton 1998). Oil Shale mining began later in the 1860s (Sneddon et al. 1938). Both the coal and oil shale industries' production peaked in the first decades of the 20th century followed by a steady decline and closure in the second half of the century. The final oil shale mine, the Westwood mine, closed in the early 1960s, and the last remaining coal mine, Polkemmet, closed in the mid 1980s. The most striking visual reminder of the past mining activities in the catchment today are the huge red oil shale wastes (Figure 1.2), known locally as 'Bings', a by product of the Scottish Shale Oil Industry.



Figure 1.2- The Greendykes Oil Shale Waste 'Bing' is shown to dominate the skyline of West Lothian; photo taken north of Broxburn looking towards the east. The red colouration of the waste is typical of oil shale waste sites in West Lothian and is related to an abundance of hematite; a consequence of the heating process used to extract oil from the shale.

The coal and oil shale industries brought significant economic and social progress to West Lothian and Scotland; however, they also had significant environmental impacts which continue to the present day. Historically, waste waters from mines, coal washing, oil shale processing sites and new mining villages were discharged directly into the Almond River. In the late 19th and early 20th century a number of reports were written, principally by medical and public health officers, indicating the scale of pollution issues along the length of the Almond River and its significant impact on river ecology (Brock 1892, Pollard 2001). The abandonment of mining in the second half of the 20th century has resulted in the widespread and uncontrolled discharge of contaminated mine waters which continues to the present day. As a result water quality in the Almond Catchment is amongst the worst in Scotland

(Pollard 2001). SEPA's 2009 Water Framework Directive classification rated all baseline ($>10\text{km}^2$ catchment area) surface water bodies as poor for ecological status and the two groundwater bodies, the 'Stirling and Falkirk bedrock and localised sand and gravels aquifers' and 'Edinburgh and Livingstone bedrock and localised sand and gravel aquifers', as poor for chemical status (SEPA 2011).

Attempts have been made in recent years to try to deal with some of the impact of historic mining activities. Passive reed bed or mixed passive reed and active pumped mine water remediation schemes have been constructed at four abandoned mine sites in the catchment (Heal & Salt 1999, Banks & Banks 2001, Heal et al. 2006). These schemes provide local improvements in water quality; however, catchment water quality remains significantly impacted.

1.3 Scottish institutional context

The Scottish water environment is an invaluable resource and asset for the Scottish population and economy; however, it could be argued that the protection of this asset has to some extent been overlooked both historically and presently. This is possibly because of the perception of water in Scotland as being abundant and of high quality created by its relatively wet climate and the traditional image of pristine and picturesque Scottish lochs, rivers and burns. For large areas of Scotland, particularly the North and North West this perception is well founded and reflects the reality. In the urbanised and industrialised Central Belt and agriculturally dominant east coastline, however, this is not the case. In these areas, which are also the main population areas, land use and anthropogenic influences, both modern and historic, have led to significantly reduced water quality (Robins 2002, MacDonald et al. 2005).

Mining is one of the principal threats to the quality of groundwater and surface water in the Scottish Central Belt (Marsden et al. 1997, Younger 2001). Unlike with other water quality threats such as diffuse agricultural pollution, landfills and contaminated land where the current or previous land owner is held wholly or partially responsible, the Coal Authority and SEPA have inherited responsibility for the vast majority of

abandoned mines. This has created a less than ideal situation where those who have assumed responsibility for a serious environmental issue also regulate the response to the issue. There is, however, a definite legislative and practical will within SEPA and the CA to deal with the impact of abandoned mines, as shown by the implementation of several large mine water remediation schemes (Banks & Banks 2001).

The European Union's Water Framework Directive (EU WFD) requires that surface water and groundwater reach 'good' status by 2027. The scale of historic mining and the impact of associated mine water contamination in Scotland, and the rest of the UK, is likely to prevent the achievement of 'good' status in the large majority of heavily mined regions. A provision has been made in the EU WFD for exemptions to be put in place where it is 'unreasonably expensive to achieve good status', however, every effort should still be made to minimise anthropogenic impact on the water environment.

A recent report 'Abandoned Mines and the Water Environment' published by EA, SEPA and CA highlighted, amongst other things, the need for;

- Catchment scale assessment of mine water contamination
- Improvements in strategy for dealing with non-coal mines
- Improvements in existing monitoring networks to consider the impacts of mine water.

This thesis aims to respond to these identified needs through the investigation of the Almond Catchment.

1.4 Environmental assessment framework

The source-pathway-receptor concept, outlined below, is central in modern environmental legislation and is also the recommended screening methodology in the Water Framework Directive (Ó Dochartaigh et al 2005). Within this thesis this concept will be used to define the potential impact of historic mining activities.

Identification of an impact on the environment or more specifically on the water environment requires that a source, a pathway and a receptor be present, this is often referred to as a 'pollution linkage'.

Source- is defined as an anthropogenic activity which poses a risk to water quality; this can include, amongst others, waste disposal, urban development, farming and mining (Ó Dochartaigh et al 2005). Although in the case of mining it is in-fact the non-activity following the mining activity, i.e. the mine abandonment, which results in the main pollutant mobilisation. The focus of this research is the impact from historic mining; potential sources include mine water discharges, subsurface mines, mine waste (bings) and diffuse mine pollution.

Pathway- this is the route by which a contaminant source acts upon the receptor. This can include movements through superficial and solid geology via intergranular and fracture flow in addition to the dispersal of mine related contaminants within river systems. Often geological and man-made features cause the creation of what are termed ‘preferential flow paths’, which include fractures and faults, areas of higher permeability material and subsurface mine voids.

Receptor- this is the body which may potentially be impacted by contamination. The receptor changes dependent upon each scenario or assessment. Common receptors are humans, eco-systems, groundwater and the wider environment. In most UK risk assessments for contaminated land the receptor is human health or groundwater. This research will consider the principal receptor to the whole water environment including groundwater and surface water.

1.5 Thesis guide

Chapter 2 outlines current mine water literature and gives a general overview of the contaminant issues and water quality impacts associated with mining and mine waste. The Oil Shale Industry’s history and legacy of potential contamination issues are discussed in Chapter 3. The scale and distribution of mining activities in the whole catchment is outlined in Chapter 4 with the presentation of a GIS map together with water quality analysis from surface waters across the catchment. This chapter sits within the thesis as a stand-alone journal paper which is currently in press with the journal ‘Applied Geochemistry’. Detailed examinations of 4 different mine sites,

representing the range of mine waste in the Almond Catchment, are presented and discussed in Chapter 5. Stratified samples of mine waters across a range of mine sites are presented in Chapter 6, their chemistry and potential hazard is analysed and a detailed hazard map for the whole Almond catchment is presented and discussed. The findings of the research, a catchment conceptual model synthesising the thesis and areas of further work are discussed in Chapter 7.

Chapter 2

Literature Review

2.0 Introduction

In this Chapter a review of available literature in the field of mine water, mine waste and mining is presented. Principally this serves to establish an understanding of the potential environmental issues associated with mine abandonment. This is a precursory requirement for the catchment scale approach to mining impacts presented in the chapters which follow. In addition, previous work conducted within the Almond catchment is reviewed, together with important regulatory guidance on the topic of mine water and water management. Some attention is given to the study of oil shale studies in other countries and the similarities between oil shale and coal, however, a comprehensive review of the history of oil shale Scotland is presented in Chapter 3.

2.1 Geology of the Almond Catchment

The Almond Catchment is located in Midland Valley which is the comparatively low lying land defined by the Highland Boundary Fault to the north and the Southern Uplands Fault to the south. These faults produced an ancient graben basin, in which a great thickness of Devonian and Carboniferous aged sedimentary rocks were deposited in a variety sedimentary environments, influenced by regional scale tectonic subsidence (Francis 1983, Cameron and Stephenson 1985, Browne et al. 1999). Extrusive and intrusive volcanic rocks are also found in the region. Outlined in Figure 2.1 and Table 2.1 is the sedimentary geology of the Almond Catchment.

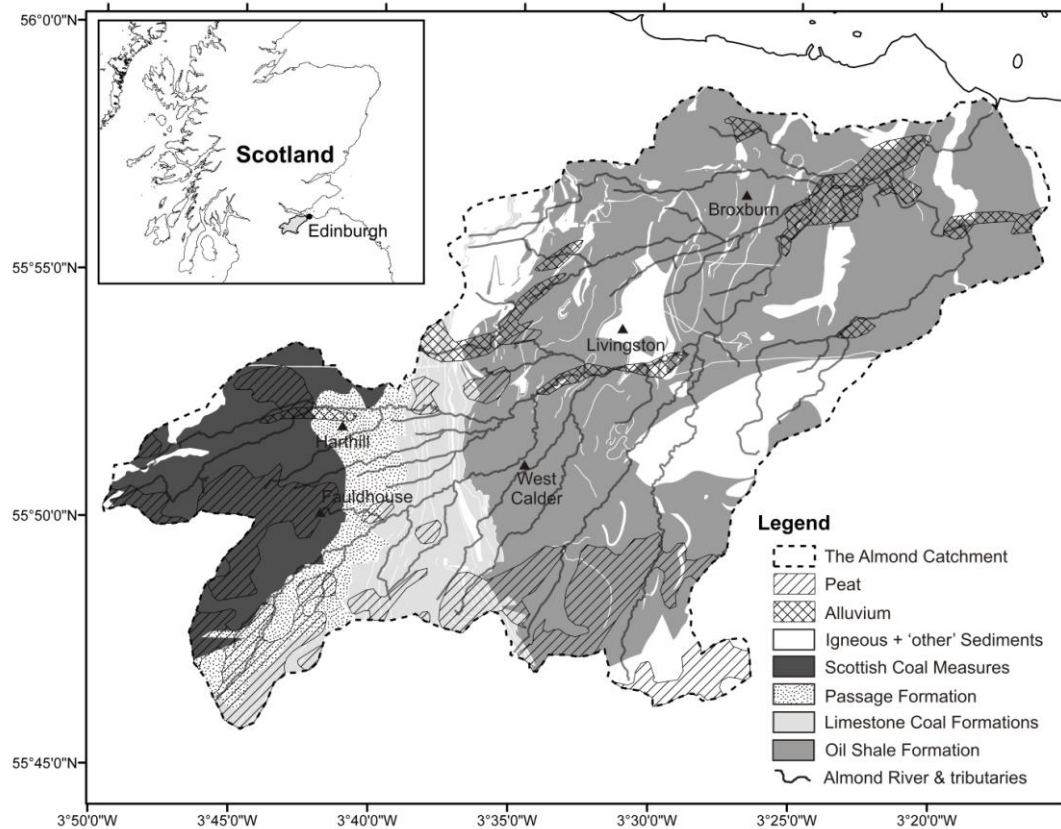


Figure 2.1 – The sedimentary geology of the Almond River Catchment is shown together with the Almond River and its tributaries as well as selected superficial geologies- peat and alluvium. The catchment geology is dominated, in the central and east, by coal measure type rocks consisting of interbedded sandstones, mudstones, shales, coal, occasional limestones and seat earths. The rocks of the oil shale formation to the west are similar but also contain up to 20 discrete seams of oil shale. Derived from BGS digital geological mapping at 50,000 scale, British Geological Survey © NERC. Contains Ordnance Survey data © Crown Copyright and database rights 2012

Period	Group	Formation	Description	Map Reference
Upper Carboniferous	Coal Measures (Scotland)	Middle Coal Measures	Cyclic sequences of sandstones, siltstones, mudstones, ironstones, coals and seatrocks	Coal Measures
		Lower Coal Measures	Cyclic sequences of sandstones, siltstones, mudstones, ironstones, coals and seatrocks	
	Clackmannan Group	Passage Formation	Mainly sandstones with fireclays and thin siltstones, mudstones, ironstones and thin coals	Passage Sandstones
		Upper Limestone Formation	Cyclic sequences of sandstones, siltstones, mudstones, marines limestones and a few coals	Limestone Coal Formations
		Limestone Coal Formation	Cyclic sequences of sandstones, siltstones, mudstones, ironstones, coals and seatrocks	
		Lower Limestone Formation	Cyclic sequences of sandstones, siltstones, mudstones, marines limestones and a few coals	
Lower Carboniferous	Strathclyde Group	West Lothian Oil Shale Formation	Mainly sandstones with siltstones, mudstones and oil-shales, thin coal seams and limestones	Oil Shale Formation
		Gullane Formation	Sandstone, grey and green, siltstone and mudstone	'Other Sediments'
	Inverclyde Group	Ballagan Formation	Sandstone, grey and red, siltstone, mudstone and dolomitic limestone	
		Kinneswood Formation	Sandstone, pink, red-brown and white with siltstone and mudstone	

Table 2.1- The Sedimentary geology of the Almond River Catchment as shown on Figure 2.1(after Cameron and Stephenson 1985, Browne et al. 1999)

The majority of the sediments found in the Almond are Carboniferous in age and were formed in a variety of humid sedimentary environments when Scotland occupied equatorial latitude. The principal coal bearing units in the region are the Middle and Lower Coal Measures and Limestone Coal Formation (Figure 2.1, Table 2.1) formed in a large fluvial-deltaic system which deposited mud and sand in variable layers, due to changing rates of delta progradation and tectonic subsidence (Browne et al. 1999). Limestone beds within the Coal Measures and Limestone Coal Formation are rare and when present form distinct lithostratigraphic markers. This is significant because it indicates that the principal coal bearing units are lacking in the main calcite, CaCO_3 , and dolomite, $\text{CaMg}(\text{CO}_3)_2$, bearing lithologies. Iron bearing carbonates, siderite, FeCO_3 , and ankerite, $\text{Ca}(\text{Mg,Fe})(\text{CO}_3)_{2(s)}$, are known to occur in significant quantities in coal bearing sequences either in mudstones and sandstones or, in the case of ankerite, on coal cleat surfaces (Hawkes & Smythe 1937, Smythe & Dunham 1947). Younger (2004) noted the significance of this in terms of the carbonate buffering potential of Wesphalian (Mid-Upper Carboniferous) aged coal measures; siderite offers no overall acidity consumption while ankerite offers some, but at much lower levels than calcite or dolomite. While it could be argued that this association was predominantly in reference to the English coal fields the lithological descriptions of Browne et al. (1999) support Younger's (2004) assertion that Fe

bearing carbonates are likely to be more abundant than calcite or dolomite. The geochemistry of carbonate buffering reactions is outlined in section 2.4.

The Upper and Lower Limestone Formations contain a more dominant carbonate component due to extended periods of inundation by the sea resulting in the dominance of limestone. Coals were formed on the edges of the seas and fluvial systems by forests, swamps and peat land. The West Lothian Oil Shale Formation represents changes between lagoonal, lacustrine and shallow marine environments. The organic rich oil shales were able to form due to the stagnation of the lagoon, during periods of extended isolation, which promoted the deposition and preservation of organic matter washed in from surrounding terrestrial environments (Moore 1968, Cameron and Stephenson 1985, Follows & Tyson 1998, Browne et al. 1999). A more comprehensive description of oil shale geology and depositional mode is present in Chapter 3.

The coals and oil shales deposited in these environments were exploited extensively during and following the industrial revolution (MacGregor et al. 1923, Carruthers et al. 1927) up until the latter half of the 20th century. This resulted in poor water quality throughout the Almond River Catchment. Outlined in the following sections are the processes and mechanism which facilitate this poor water quality through the release of mine water pollution.

2.2 Acidic mine drainage and sulphide oxidation

The production of contaminated mine waters from active and abandoned mine sites is a well documented phenomena around the globe. The principal contaminants encountered in coal mine waters are elevated levels of proton acidity, H^+ , elevated metal concentrations, principally Fe, Mn, Al, Ni and very high concentrations of sulphate, SO_4^{2-} , often collectively termed Acid Mine Drainage (AMD) (Wood et al. 1999; Chen et al. 1999; Younger 2000, 2001; Banwart & Malmström 2001; Banks et al. 2001, Blowes, 2003, España et al. 2005, Akcil & Koldas 2006, Gzyl et al. 2007). The use of term acidic mine drainage (AMD) is potentially misleading, particularly to those not familiar with mine water chemistry, as often waters are net-alkaline with

circum neutral pH (Younger 1995b, Banks et al. 1997b, Younger 2001, Cidu et al. 2009); nevertheless the term is used almost ubiquitously in the literature to describe polluted discharges from mine sites. Iron is commonly the most abundant metal contaminant in mine waters however more eco-toxic metals such as Cd, Ni, Zn, Pd and Hg do also occur, particularly in areas which have been mined for metal and metals ores (Cidu et al. 2001).

The oxidation of sulphide minerals, principally pyrite, FeS_2 , is the primary trigger for the production of mine water contamination (Stumm & Morgan 1981, Backes et al. 1986). Other sulphide minerals such as, marcasite (FeS_2), pyrrhotite (Fe_{1-x}S), mackinawite ($(\text{Fe,Ni})_9\text{S}_8$), covellite (CuS), millerite (NiS) and galena (PbS) may also facilitate acid generation with the coincidental mobilisation of metals such as Ni, Cu and Pb (Lottermoser 2010). Sulphide minerals with low or no Fe content do not have the same acid generation capacity as Fe rich sulphides (Plumlee 1999). Furthermore, sulphide minerals often contain minor or trace elements bound within their crystal structure (Table 2.2), due to cation substitution, which may be mobilised during oxidation/dissolution reactions (Vaughan & Craig 1978, Lottermoser 2010).

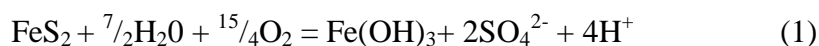
Mineral name	Chemical Formula	Minor and trace element substitution
Arsenopyrite	FeAsS	
Chalcopyrite	CuFeS_2	Ag, As, Bi, Cd, Co, Cr, In, Mn, Mo, Ni, Pb, Sb, Se, Sn, Ti, V, Zn
Cubanite	CuFe_2S_3	
Galena	PbS	Ag, As, Bi, Cd, Cu, Fe, Hg, Mn, Ni, Sb, Se, Sn, Ti, Zn
Marcasite	FeS_2	As, Hg, Se, Sn, Ti, Tl, Pb, V
Millerite	NiS	
Pyrite	FeS_2	Ag, As, Au, Bi, Cd, Co, Ga, Ge, Hg, In, Mo, Ni, Pb, Sb, Se, Sn, Ti, Tl, V
Sphalerite	ZnS	Ag, As, Ba, Cu, Cd, Co, Cr, Fe, Ga, Ge, Hg, In, Mn, Mo, Ni, Sb, Se, Sn, Ti, V

Table 2.2- Selected sulphide minerals, their chemical formula and the minor and trace elements which have been identified to be constituents of their mineral structure due to cation substitution. Dissolution and oxidation of these minerals, often accelerated due to initial pyrite oxidation, act as one of the main source of contaminants discharged in mine waters (after Vaughan & Craig 1978, Lottermoser 2010).

Mining processes facilitate sulphide oxidation by the introduction of oxygen in to previously anoxic environments (Banks et al 1997a, Younger 2004). This involves either lowering of groundwater levels in a subsurface mine or by discharging mine overburden material at surface (Wiggering 1993, Nordstrom 2009). Pyrite is generally the most common sulphide mineral in coal measure rocks (Gzyl et al

2007), particularly in argillaceous rocks where anoxic depositional environments may promote the formation of pyrite (Kolker and Huggins 2007, Lottermoser 2010).

The overall pyrite oxidation process at a mine site can be simplified and expressed as a single equation;



In this equation the introduction of oxygen, O_2 , to the previously reduced environment leads to the production of solid ferric hydroxide, Fe(OH)_3 , dissolved sulphate, SO_4^{2-} , and proton acidity, H^+ (Younger 2000, Banwart & Malmström, 2001, Rimstidt & Vaughan 2003, Lottermoser 2010). In practise, the majority of pyrite oxidation, in the mine, is caused by indirect oxidation involving micro-organism, oxygen and dissolved Fe (Larsson et al. 1990). Abiotic oxidation of pyrite in the natural environment is not common (Evangelou and Zhang 1995, Lottermoser 2010). The cycle of pyrite oxidation reactions which can occur at mine sites is illustrated in Figure 2.2.

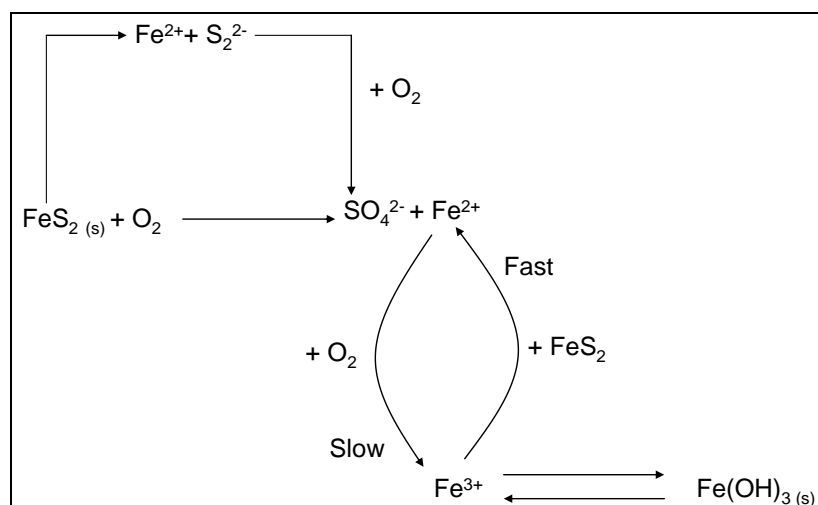


Figure 2.2 - Simplified diagram illustrating the reaction pathways for pyrite oxidation. Pyrite is oxidised by dissolved oxygen producing SO_4^{2-} and Fe^{2+} which is further oxidised to produce Fe^{3+} which forms Fe precipitates during discharge at surface. However, the oxidation of pyrite is greatly accelerated by the presence of Fe^{3+} in solution leading to much more rapid release of acidity and contaminants and greater environmental impact. (after Stumm & Morgan 1981, Arnesen 1993, Banks et al 1997)

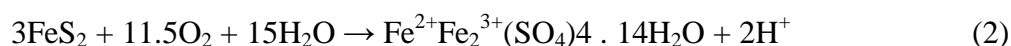
Following pyrite oxidation, either by oxygen or Fe^{3+} , the majority of the Fe released into mine water will generally remain in a dissolved state dependent upon the prevailing redox conditions (Garrels & Christ 1965), oxygen and pyrite availability in the mine. Only when waters are discharged at surface does $\text{Fe}(\text{OH})_3$ formation commonly occur, due to the increased availability of atmospheric oxygen. This results in the orange coating, observed around the globe, on stream and river beds receiving discharge waters from historic mine sites. The precipitation of Fe as $\text{Fe}(\text{OH})_3$ is the principal cause of environmental damage associated with mine water discharge as $\text{Fe}(\text{OH})_3$ smothers the river bed, preventing light infiltration, reducing the production of photo synthesisers, reducing dissolved oxygen levels and leading to ecological impoverishment (Jarvis and Younger 1997). However the process of contamination production at mines and the associated environmental impacts are even more complex than the above description implies.

2.3 Storage of acidity

In the majority of mines and mine wastes pyrite oxidation is not permitted to run to completion as the movement of the reaction products, away from the reaction site, into the saturated zone is limited, principally by the availability of water (Younger 2001, Gzyl et al. 2007). Proton acidity, sulphate and iron produced may initially move into pore waters (Gzyl et al, 2007), however, water quickly becomes saturated and, in subsurface mines, is unlikely to be replenished during the active mining phase. Consequently intermediate solid phases of ferrous/ferric hydroxyl-sulphate evaporate minerals collectively termed acid generating salts (AGS) are formed in the mine (Bayless & Olyphant 1993, Lin 1997, Lin & Herbert 1997, Younger 2000, Lottermoser 2010). Examples of these acid generating salts include;

- Melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)
- Romerite ($\text{Fe}_3(\text{SO}_4)_4 \cdot 14(\text{H}_2\text{O})$)
- Coquimbite ($\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9(\text{H}_2\text{O})$)
- Copiapite ($\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20(\text{H}_2\text{O})$)
- Potassium Jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$)
- And other Jarosite family salts

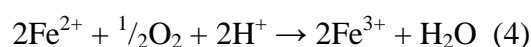
The formation of AGS minerals in the operational period of the mine site influences the impact, timing and magnitude of contaminant release (Younger 2000). It is well documented that mine waters pumped during the operational period of most mine sites generally contain significantly lower contamination concentrations (Fe, SO₄, H⁺ and other heavy metals) than discharge waters following rebound (Cairney & Frost 1975, Banks et al. 1997a, Wood et al. 1999, Younger 2000, Gzyl et al 2007). This difference can in part be accounted for due to the formation of AGS. Younger (2000) uses the example of the formation of Romerite from partial pyrite oxidation:



When compared to reaction (1) the amount of proton acidity released relative to the amount of pyrite consumed is lower in reaction (2). Therefore reaction (2) produces less acidity than reaction (1), and effectively stores acidity by the formation of acid generating salts (Younger 2000). When pumping ceases in the mine and mine waters begin to rise within workings, Romerite and other AGS formed are rapidly dissolved, releasing ferrous and ferric iron into solution (Younger 2000). The ferric iron, Fe³⁺, released can react with water to partially release the proton acidity, which was stored in the AGS, via reaction (3).



The ferrous iron released into solution is coincidentally oxidised according to equation (4) (Banwart et al. 2001) consuming dissolved oxygen in solution;



Most of the rebound in mine sites occurs due to the direct infiltration of oxygen rich surface waters and rain waters (Nuttall & Younger 2004) causing an abundance of dissolved oxygen to mediate reaction (4). It should be noted that reaction (4) consumes proton acidity, however the difference in the ratio between the proton acidity consumed to produce ferric iron and the ratio between the hydrolysis of ferric iron and the release of proton acidity results in a net increase in proton acidity

in solution. This net increase accounts for the proton acidity previously stored by the AGS formation.

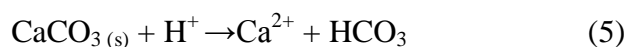
There is often a significant time lag between equations (2), (3) and (4) meaning that the formation of the AGS stores acidity in the unsaturated zone (Younger 2000). This time lag is effectively the difference between the commencement of the operational mine period and groundwater rebound phase in a subsurface mine. It is common to find that the AGS dissolution can result in an increase in dissolved iron concentrations by two orders of magnitude and a drop in pH of 3 units in discharging waters (Younger 2000) a process referred to as ‘geochemical trauma’ or ‘first flush’(Younger 1997).

2.4 Attenuation of acidity

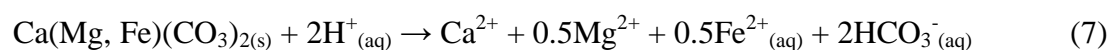
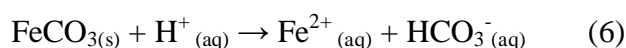
The oxidation chemistry of pyrite in subsurface mines and mine waste results in low pH waters with elevated concentrations of Fe and SO₄. The low pH allows the mobilisation of other heavy metals, common examples include Al and Mn and also, particularly in Scottish mine waters, Ni (Younger 1997, Younger and Sapsford 2004). However, mine water discharge at surface is often pH neutral, contains an excess of alkalinity and is therefore classified as net alkaline (Hedin et al. 1994, Younger 1994, 1995, 2000, 2001, Banks et al. 1997b, Jarvis and Younger 1997). This is due to the consumption of proton acidity by the dissolution of carbonate and silicate minerals in the mine which provide natural attenuation and buffer mine water pH (Blowes & Ptacek 1994, Stomberg & Banwart 1999, Banwart et al. 2001, Lottermoser 2010). Commonly the availability of buffering minerals, in the whole mine complex, is higher than acid generating minerals, furthermore, acid generation is limited by the availability of oxygen whereas buffering reactions continue, without oxygen, following groundwater rebound.

Calcite and dolomite are abundant in limestone, mudstone and other sedimentary rocks commonly found in mine strata found around the world. Although, as mentioned previously, they are less dominant in the main coal bearing units of the Westphalian Coal Measures of northwestern Europe (Younger 2004). Crushed

limestone was also commonly used as a fire suppressant in subsurface mines potentially adding to the buffering capacity of certain mine complexes. If we consider calcite weathering in the mine;



Proton acidity, H^+ , released by pyrite oxidation is consumed in the dissolution of calcite, CaCO_3 , increasing the pH of water and dissolved calcium, Ca^{2+} , and bi-carbonate, HCO_3^- , concentrations. The chemistry is similar for dolomite weathering reactions which also consume acidity but release magnesium, Mg^{2+} , in addition to calcium ions. Iron carbonates, siderite, FeCO_3 , (eq. 6) and ankerite, $\text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2$, (eq. 7) may also consume proton acidity but the coincidental release of Fe will generally negate the buffering action as subsequent Fe hydrolysis (eq.3) will remobilise most, if not all, of the previously consumed acidity (Younger 2004).



Common silicate minerals which consume acidity, although generally at a lesser rate than carbonates, include biotite, K-feldspar, albite and kaolinite (Banwart & Malmström 2001, Lottermoser 2010). The natural attenuation of proton acidity in workings by buffering reactions is a crucial influence on the contaminant potential of mine waters as the bio-availability and mobility of metal ions is heavily pH dependent (Banwart & Malmström 2001). While buffering reactions increase pH of mine waters, therefore reducing the mobility of some metals, Fe concentrations are still recorded at very high levels (>50mg/l) in some circum-neutral mine waters (Younger 2001). Presumably this is partially exacerbated when much of the acidity buffering comes from Fe carbonates which coincidentally release Fe. Also, the result of buffering reactions is that mine waters can become extremely mineralised, showing very high conductivity values. Furthermore while silicate buffering reactions consume acidity the associated release of aluminium, Al, acts as the principal source of Al in mine water (Banwart and Malmström 2001, Younger 2004).

2.5 Variability in mine water discharge composition

The timing and relationships between pyrite oxidation, secondary mineral formation and carbonate buffering reactions all influence the contaminant potential of mine waters; however contaminant concentrations are also influenced by several other factors. Mine waters from subsurface flooded mines evolve over time and contaminant concentrations generally reduce from high levels at the point of first emergence to a lower asymptotic level (Wood et al, 1999). The processes which affect the evolution of mine water chemistry were classified by Wood et al (1999) as follows;

Time Independent Factors

- The lithological setting of coal bearing strata can impact the concentrations of contaminants released from a mine site. Coals more closely associated with marine deposition generally contain higher sulphur and pyrite content (Spears et al. 1999) than non-marine influenced coals resulting in higher contaminant concentrations in discharge waters (Caruccio & Fern 1974, Younger & Adams 1999).
- The size of the subsurface mine complex can also influence discharge contaminant concentrations; larger mine systems are likely to have a larger surface area of strata in which pyrite can be oxidised.

Time Dependent Factors

- The transition from ‘vestigial’ to ‘juvenile’ acidity (Younger 1997). Vestigial acidity arises from contaminants being mobilised by the oxidation of pyrite within the mine complex which leads to contaminated pore waters and secondary mineral formation (AGS). These contaminants are flushed out from the mine site relatively quickly when pore water contaminants move into groundwater and secondary sulphate minerals (AGS) are quickly dissolved giving high initial contaminant concentrations in discharge waters. Juvenile acidity is contamination derived from pyrite oxidation, following groundwater rebound, in the zone of seasonal groundwater fluctuations. In

general the availability of pyrite in this zone is limited compared to the whole mine complex.

- Carbonate dissolution. Following the formation of acidity from pyrite oxidation; carbonates present within the workings buffer pH and increase alkalinity. While acidity production is limited by the availability of oxygen, buffering processes are not and so can dominate more readily in the flooded mine complex (Banks et al, 1997).
- The bacterial reduction of sulphate. Bacteria consume sulphate and increase bicarbonate alkalinity. This only occurs in anoxic ground waters following water table rebound.
- Change in flow rate through time results in the dilution or concentration of contaminants.

These influences were demonstrated by a temporal study of mine water chemistry for 32 mine discharges in the Midland Valley of Scotland. Indicating that mine water pH is rarely acidic and that discharges which were slightly acidic, at first emergence, progressed to circum-neutral pH within 30 years (Wood et al. 1999). Alkalinity was variable but generally high and then declining after 25 years, Fe concentrations were wide ranging for the first 40 years but always declining to below 30 mg l^{-1} (Wood et al. 1999). This study showed that there are definite trends in the evolution of mine waters over time between sites. It seems, however, that the difference in Fe and SO_4^{2-} concentrations may be due to dilution processes within individual mine sites (Wood et al. 1999). The dilution impact is likely to be greatest where the mine workings volume is small, the hydraulic conductivity of the mine is high and the recharge rate is high (Wood et al. 1999)

Dilution may be a significant influence on the variability in concentrations between different mine sites, however, there are also geological controls on mine water chemistry. The distance between the discharge point and the 'mostly closely associated coal seam' (MCACS) has been shown to influence discharge chemistry. Also, the proximity of the coal seam to a 'marine' bed has been shown to have a significant influence on discharge chemistry (Younger 2001). In a study of Scottish

mature mine water discharges only discharges within 0.5 km of the MCACS exceeded 20mg/l of iron (Younger 2001). (A mature discharge is a discharge in the juvenile acidity stage and so contaminant concentrations are produced from pyrite oxidation in the zone of water table fluctuations.) A similar relationship was shown for pH but the results were less clear cut. However, pH values below 6.5 can only be expected within 0.5km of the MCACS outcrop (Younger 2001). Also discharges in excess of 100mg/l Fe are likely only where there is a 'marine' bed within 25m of the MCACS. Where the 'marine' bed is more than 80m stratigraphically above or below the MCACS then discharges below 4mg/l Fe should be expected (Younger 2001).

The pyrite content of the worked and surrounding strata of a mine site is likely to be one of the principal controls on Fe concentrations in waters. The initial high contaminant concentrations (up to 400mg/L) associated with mine discharges is referred to as vestigial acidity and is caused by the flushing of contaminants stored in the mine from the active mining phase (Younger 2000) This vestigial acidity phase lasts approximately 40 years during which time iron concentration decay exponentially to an asymptotic concentration of around 10-30mg/L referred to as the juvenile acidity phase (Younger 1997, 2000). The length of the vestigial acidity phase or the flushing phase can be described by the equation (Younger 2000),

$$t_f = (3.95 \pm 1.2) t_r \quad (8)$$

The equation states that the flushing time (t_f) is equal to 3.95 ± 1.2 (where the \pm represents the natural variability between mine sites) times the rebound time, t_r (the length of time for the water table to rebound to be in equilibrium with the surrounding water table). The above equation was tested for coal mines sites in Poland which suggest that factors such as the porosity of surrounding strata and dissolution rates of minerals may influence the validity of Younger's relationship between rebound time and flushing time. The flushing time was found to be 10-20 times the rebound time in contrast to equation (8) which suggested a flushing time 4-5 times greater than rebound (Gzyl, 2007). However, the study in Poland was limited to single sets of mine workings as opposed to whole mine systems. Therefore, both

Younger's and Gzyl's findings may be valid depending upon the scale of the historic mining operations.

The magnitude of juvenile acidity is determined by the pyrite content of unsaturated zone stratum and by seasonal water table fluctuations leading to increases in the unsaturated zone allowing for increased pyrite oxidation (Younger 2000). Increases in pyrite oxidation are reflected in increases in proton acidity, iron and sulphate in discharge waters. Moreover, increases in dissolved Fe concentrations in mine waters allows for oxidation of pyrite in the saturated zone deeper in the mine through the oxidation of pyrite by ferric iron (Younger 2000). These observations become more significant when considered in the context of climatic change. Increases in global temperature will result in longer dry spells. Increases in the concentration of contaminants occurs in mine shafts and mine pore waters as infiltration of recharge waters is reduced (Nordstrom 2009). Precipitation following a dry spell leads to a 'First Flush' scenario where waters with high contaminant concentrations are flushed in to the wider environment, as well as water table fluctuations becoming bigger leading to more pyrite oxidation. This results in an increase in concentration of contaminants being observed on the rising limb of discharges following dry spells (Nordstrom 2009).

2.6 Morphological control on mine waters

Almost all mine sites are morphologically distinct as the individual geology of an area dictates how a resource (coal or oil shale in the case of the Almond) is mined. Mine sites can be divided in to broad categories of free draining workings, flooded workings, spoil heaps and opencast sites (Rees et al. 2002).

Flooded workings are those which show the distinct evolution of minewater chemistry due to the 'first flush' (Younger 2000) and the change from vestigial to juvenile acidity (Wood et al. 1999) as oxygen ingress into workings following rebound is limited (Rees et al. 2002). Therefore, pyrite and similar sulphide oxidation as well as the acid generating salts (AGS) formation can only occur in the unsaturated zone (Rees et al. 2002). Mine water stratification is a common feature of

flooded workings, particularly when connectivity between individual shafts is limited and recharge is dominated by surface recharge (Nuttall & Younger. 2004). A pumped working is a special case of a flooded working where by water is actively removed from a site to maintain a specific groundwater level. For historic workings this is often to prevent uncontrolled surface breakouts of mine water. This occurs in the Almond Catchment at the Polkemmet mine which is actively pumped to prevent the uncontrolled breakout of waters. These waters are then treated prior to discharge. The County Durham coal field is another high profile example of an area where active pumping is used to prevent the uncontrolled discharge of mine waters (Younger 1995).

Free draining workings are sub-surface mine workings above the water table and so water is able to move through them freely, never becoming completely flooded, also oxygen ingress is able to occur long after the cessation of mining (Rees et al 2002). There is no groundwater ‘first flush’ with free draining workings (Rees et al 2002) as the mine is always in a phase of juvenile acidity..

Spoil heaps are waste rock piles from mining which are referred to colloquially as ‘Bings’ in Almond catchment and Scotland. The processes of pyrite and other sulphide oxidation in spoil heaps is more significant than in flooded workings due to the larger surface area of deposits being exposed to atmospheric oxygen and water ingress (Rees et al 2002, Nordstrom 2011). The Almond catchment is relatively unique, in the UK, as it contains up to 150 million tonnes of oil shale waste. These ‘spoil heaps’ differ from those described by Rees et al. (2002) because the majority of the oil shale has been heated altering the mineralogy and the potential discharge chemistry. This is described in more details in Chapter 3.

In opencast workings, where mining extended below the water table, cessation of mining and pumping actives inevitably leads to the formation of a mine pit lake (Bowell 2002), if appropriate restoration is not undertaken. The same sulphide mineral oxidation reactions occur in mine pit lakes (MPL) as with other mine sites, however other biological and seasonal processes occur which are unique to MPLs.

There are two conceptual models which form the basis of understanding of the different processes which dominate in pit lakes, terminal sump and a through flow system (Bowell 2002). A terminal sump acts as an evaporation pan and is the lowest hydrogeological point in a basin. Therefore the only outflow from a terminal sump is via evaporation. A through flow system can have significant impacts as high sulphate and metal concentrations move into the surrounding groundwater (Bowell, 2002).

Rees et al (2002) investigated how morphological differences between mine sites (excluding opencast sites) are reflected in mine water discharge quality. A classification scheme which differentiated between the dominant chemical signature of different mine site morphologies was developed from the 81 mine sites investigated (Table 2.3)

Discharge Source	pH	Net Alkalinity mg/l CaCO ₃	Piper Classification
Flooded Workings	<5-8	0 to 500	Ca-Mg-SO ₄ /HCO ₃
Spoil Tip	<5	-2500 to 0	Ca-Mg-SO ₄
Free Draining Workings	5-7	80 to 180	Ca-Mg-SO ₄
Flooded and free Draining Workings	>5<8	-350 to 200	Ca-Mg-SO ₄
Pumped	6.5-7.5	500 to 1000	Na-HCO ₃ /SO ₄

Table 2.3 A summary of chemical properties associated with different mine site morphologies (Rees et al. 2002). The net alkalinity is calculated by subtracting the acidity from the alkalinity, for low pH mine waters this value can be negative as they contain no alkalinity. The piper classification is based on the dominance of major ions and is discussed later in this chapter.

A full discussion of the derivation of classes in Table 2.3 can be found in Rees et al. (2002). However, the table suggests that spoil heap waters are generally net-acidic due to the dominance of pyrite and sulphide mineral oxidation and AGS formation with limited attenuation and buffering from carbonate mineral dissolution (Rees et al. 2002). Flooded and free draining workings are net-alkaline as are flooded workings; however, flooded workings normally show greater net-alkalinity values as acid generation is limited following flooding (Rees et al. 2002). Aerobic sulphide oxidation is able to continue in free draining workings due to the abundance of atmospheric oxygen when compared to a flooded working (Rees et al. 2002). However flooded workings can also be distinguished by their HCO₃ component.

Pumped discharges being a special case of flooded workings have a tendency to exhibit Na or K and Cl components which is likely due to interaction with deep basin brine or a sea water component (Rees et al. 2002) drawn into workings. Pumping at mine sites tends to break down hydrochemical stratification in the water column which can have significant effects on the chemistry of observed discharge waters other than the inclusion of a saline component. Hydrochemical stratification of mine water column is a common phenomenon encountered in flooded mine sites (Nuttall

& Younger 2004). Stratification can result in heavily mineralised waters accumulating at the base of a water column whilst shallow waters will be significantly less mineralised. Iron or zinc (more commonly in metal mines) concentrations can be two orders of magnitude greater in the bottom of a mine shaft relative to the top (Nuttall & Younger 2004). Mixing of the shaft waters, due to pumping, means contaminant concentrations, following the discharge of one shaft water volume, can be significantly higher than those of the shallow shaft waters prior to pumping (Nuttall & Younger 2004). Stratification is a reflection of the mineralogical type, subsurface morphology and groundwater recovery rate in the mine.

While the majority of the references outlined in the above section refer to coal mines there is also evidence the same processes occur at oil shale mines in Poland (Erg 2005). To date, however, no investigations have demonstrated the impacts of mine water pollution associated with oil shale mining in the UK.

2.7 Bacterial influence on mine waters

The subsurface was for a long time considered a sterile environment however bacteria play a significant role in subsurface chemistry, particularly at mine sites. Indeed the reaction pathways previously outlined in Figure 2.2 are all generally mediated by bacteria. The role of the sulphur bacterial cycle is significant at almost every mine site due to the biogenesis of metal ores via sulphide oxidation bacteria (Natarajan, 2008). The acidithiobacillus group of bacteria aid the dissolution and mobilisation of copper, iron, zinc, cadmium, arsenic and nickel in acidic solutions from mine sites (Natarajan 2008). Pyrite oxidation has been shown to be the principal control on contaminant release from coal mine sites; however this oxidation reaction is facilitated by the acidophilic autotrophic bacteria of the acidithiobacillus group which act as a catalyst to the reactions. These bacteria use ferrous iron and sulphur compounds as energy sources for reproduction and growth (Mayes et al. 2008)

Acidithiobacillus ferrooxidans and *Acidithiobacillus thiooxidans* are ubiquitous at most mine sites and are responsible for acceleration in the oxidation of metal sulphide (Natarajan 2008). *Acidithiobacillus Ferrooxidans* is the key contributor to oxidation of pyrite at mine sites, whilst *Acidithiobacillus thiooxidans* cannot oxidise pyrite but grows through the oxidation of sulphur released following pyrite oxidation. (Natarajan 2008; Blowes et al. 2003).

Sulphate Reducing Bacteria (SRB) are also of significance at mine sites as they can effectively remove Fe, Zn and Cu as sulphide precipitates (Natarajan 2008). However this process is thought to be time dependent as SRB are established in anoxic conditions following rebound (Wood et al. 1999). It has been suggested that one of the main influences on net alkaline discharges is the result of microbial sulphate reduction in the shallow subsurface prior to surface discharge (Mayes et al, 2008)

2.8 Diffuse pollution effects

The majority of literature on the environmental impact of mining tends to focus on the point sources impacts that historic mining sites have on surface waters through mine site discharges. Studies are beginning to demonstrate that diffuse sources of contamination can be a significant contributor to contaminant levels in surface water bodies (Nuttall & Younger 1999, Mayes et al. 2008). Diffuse pollution sources in a mined catchment are described by Mayes et al (2008) as follows,

- Diffuse seepages in the immediate vicinity of point discharges
- input of contaminated groundwaters directly to surface waters via the hyporheic zone
- run off from spoil heaps
- resuspension of river bed and bank sediments rich in metal contaminants

Investigation has shown that the relative effects of point and diffuse contamination is variable dependent upon the rate of flow within the affected surface water body (Mayes et al. 2008). The rate of flow in any water course is a function of precipitation within its catchment area minus the amount of evaporation in the catchment in addition of a component of groundwater input. During low flow events in the heavily mined catchment of the River Gaunless, diffuse pollution contributes

approximately 50% of instream iron loading (Mayes et al. 2008). In low flow, it is thought the major diffuse sources of contamination come from diffuse seepage around point mine water sources (Mayes et al. 2008). During high flow events up to 98% of iron loading comes from diffuse sources, predominantly re-suspension of iron rich stream sediments.

These findings are significant in terms of assessment of instream contaminant levels in any catchment, in that the timing of water sampling relative to flow can have significant influence on contaminant loads.

2.9 Global perspective on mine pollution

Coal and oil shale mining are the most prevalent forms of mining in the Almond Catchment and the above literature review is focused on work undertaken on similarly mined areas, principally in the UK. However, globally mining includes a wide range of resources, environments and potential environmental consequences. In this section examples of mining activities from around the world are used to give a global perspective on the environmental impacts of mining.

South west Spain, the Iberian Pyrite Belt

Arguably, one of the most famous modern day examples of the environmental impacts of mining comes from the Iberian Pyrite Belt in SW Spain which includes the Rio Tinto mine. Historic metaliferous mining in the Iberian Pyrite Belt has left a legacy of abandoned mines, spoil heaps, tailings ponds and flooded pits (Espanna et al. 2005). Acidic mine drainage in this area has led to the mobilisation of dissolved metals such as Fe, Al, Mn, Cu and Zn as well as Cd and Hg (e.g. Van Geen et al. 1991) which are rarely associated with coal and oil shale mines but are a more common feature of metal mining in the massive sulphide ores in this and other metal mined areas. This mobilisation has led to severe pollution of associated fluvial systems, Tinto and Odiel, and the loss of almost all aquatic life except the extremophile microorganisms adapted to such extreme conditions (Lopez-Archilla & Amilis 1999). A study of the Iberian Pyrite belt by Espanna et al. (2005) demonstrates the extreme pH (1.4-4) sulphate (up to 44g/L) and metal concentrations

(up to 7.7 g/L Fe, 2.6 g/L Al and 1.4 g/L Zn) associated with AMD from the numerous mine sites in this area. Due to these extreme discharges rivers in the region exhibit variable colours related to the precipitation of AGS and Fe precipitate minerals such as jarosite, schwetmannite and ferrihydrite (Espanna et al. 2005). Such extreme discharges are not encountered in the Almond, however, the link between aquatic bio-diversity, AMD and the precipitation of Fe and AGS minerals might be significant on more local scales in the Almond.

Romanian Metal Mining

The Matamues and Saty Mare Counties in Romania offer a less extreme but potential more significant example, due to direct human impacts, of metal mining which has resulted in significant contamination of a number of river catchments with elevated concentrations of Cd, Cu, Pb and Zn. This has been shown to have significant implications for potable water supplies, particularly in rural areas (Bird et al. 2009). Metal mining in these areas is related principally to hydrothermal vein mineralization associated with volcanic rocks which contain deposits of Cu, Pb, Zn, Au and Hg. The pH, Eh and bedrock geology in mined areas was found to influence the solubility of metals in groundwaters which peaked at 31 µg/L Cd, 50 µg/L Pb and 3000 µg/L in some catchments; lower levels were recorded elsewhere related to lower loading from mining and other industrial sources. The concentrations of metal contaminants are of potential concern to human health and are likely to result in a less than 'good' EU Water Framework Directive groundwater status (Bird et al 2009).

Copper and zinc mining, Norway

Mining for Cu, Zn, from ores, and S, from pyrite, in the Caledonian mountain chain (mid-Norway) has resulted in the discharge of Cu, Zn, Fe, Pb and Cd contaminated mine waters and the classification of rivers in the region as 'significantly' or 'highly' polluted (Schartau 1992, Banks et al. 1997a) The main issue is related to pollution from subaerial mine waste tips containing high abundance of sulphide minerals; a consequence of in-efficient extraction practices associated with the historic copper and zinc mining (Banks et al. 1997a). Mining induced contamination has caused the loss of fish from some rivers while spoil tips and the fill of deep mines with

significantly contaminated waters presented significant problems in other areas. Indeed waters from this mining area previously represented Norway's single largest emission of Cu and Zn (Banks et al. 1997a)

Sardina, Italy, Lead and Zinc Ore Mining

Cessation of dewatering activities associated with the Pb-Zn mine in Sardina Italy resulted in significant increases in salinity, principally Na and Cl, and Hg concentrations in overlying aquifers due to mixing in the shallow groundwater system (Cidu et al. 2001). Here as apposed to contaminant being sourced solely from the mining activity in isolation the increases in Cl facilitated the dissolution of Hg. The saline waters were drawn into the mine complex, due to intensive pumping, from the adjacent Mediterranean Sea. Clearly this example emphasises the importance of geological conceptualisation in understanding the potential implication of mining when saline intrusion in to the mine can increase the potential for mine related pollution effects. This component of increase in Cl dominance in mine waters due to saline intrusion into mine complexes is also demonstrated in Glover (1983) for pumped mine waters in the UK, which Younger (1995) incorporates into the now widely used mine water classification scheme.

Chile, Mine Waste and Climate

The response of contaminant mobilisation from surface mine wastes in different climatic regimes in Chile was demonstrated by Dold & Fontbote (2001) by the investigation of three mine wastes sites. They indicated the significance of leachate mobilisation of metal contaminants from pyrite oxidation and AGS in precipitation-dominated climates, as is also the case in Scotland. The alternate scenario presented indicates that in climates where evaporation exceeds precipitation upwards migration of waters via capillary forces results in secondary sulphate/AGS being concentrated to the top of the waste pile (Dold & Fontbote 2001). While the second scenario is unlikely to occur in Scotland, it does indicate that role of climate is significant in contaminant mobilisation, a fact which may become more significant in mined areas vulnerable to climate change in the future.

Scotland in 2013

Mining in the UK is largely abandoned with only limited deep coal mining undertaken in Yorkshire and surface coal operations undertaken in Scotland. However, abandonment issues are still very much at the fore as in 2013 two of the largest surface coal mine operators went into liquidation leaving numerous un-restored surface coal sites across central Scotland (Ayrshire, South Lanarkshire and Fife) (Paul Butler, SEPA, personal communication). Indeed, the author is currently involved in the regulatory response to this issue in terms of the prioritisation of those sites, where mine waters are quickly rebounding due to the cessation of pumping, in terms of the likely environmental and water quality implications. While the majority of these sites display relatively low sulphide contents, suggesting only moderate contaminant mobilisation and would be considered of low significance compared to the above examples, some notable exceptions exist. For example, there are on going issues associated with Europe's largest bituminous coal mine pit lake in Fife (see Younger 2005 for a historical perspective) and also some serious potential water quality issues associated with a site close to Douglas, in South Lanarkshire, which contains pyrite up to 16 wt% where groundwater is currently rebounding and which will, without intervention, result in direct discharge to the Douglas Water.

2.10 Previous work in the Almond

The availability of previous studies in the Almond Catchment is limited, although some notable examples include works on the influence of anthropogenic activities on catchment water quality (Pollard et al 2001), a paper on the potential impacts associated with uncontrolled discharge at the Polkemmet Mine (Chen et al. 1999) and some work undertaken on the oil shale bings from ecological perspective by Harvie (2004, 2005). Also, two studies on mine waste remediation have been undertaken in the catchment one on an ironstone waste (Heal & Salt 1999) the other on a discharge from a former coal colliery spoil.

SEPA have undertaken several pieces of work which provide an over view of the environmental condition of surface water bodies in the catchment as well as general information on the role of contaminant sources (e.g. SEPA 2008) The review by

Pollard et al. (2001) documents the ecological impact of historic mining inputs, urban development and other industries on the River Almond. It indicates that before 1864-65 fish stocks within the Almond River were abundant. Legal proceedings with regard to the quality of the river revealed that between 1872-1875 no fish could be observed within the Almond. Again in 1935 the 'Department for Health in Scotland' report no fish in the river (Pollard et al. 2001). The first major breakout of Acid Mine Drainage began polluting the Breich Water (major tributary of the Almond) in 1983, however, the impact of mining could be seen long before this with black coal solids along the length of the river in 1935 (Pollard et al. 2001). It was reported that due to breakouts and leachates from bings dissolved oxygen levels in the river plummeted (Pollard et al. 2001).

Research by Chen et al. (1999) into specific mining sites provides the most useful information with regard to deep mining inputs into the catchment. The study focuses principally on the Polkemmet and Riddochhill collieries; the deepest and volumetrically most significant mine sites in the catchment. Mining ceased at these sites during the 1980s. In the 90s groundwater recovered at a rate of 0.15-0.2m/week. Based on this, predictions suggested that discharges would start to impact the Almond around 2000 (Chen et al, 1999). Chen et al. (1999) showed, via investigation of two of the major mineshafts in the region, the geochemical progression from recharge water chemistry to that of that of the recorded chemistry in flooded mine shafts. Investigation and NETPATH modelling at Riddochhill and Polkemmet showed that pyrite oxidation, calcite dissolution and goethite precipitation were of principal influence on the chemistry of the two shaft waters (Chen et al, 1999). However, it also indicated that modelled mineral dissolution rates were significantly more rapid in the Riddochhill shaft than Polkemmet, primarily due to the difference in the availability of dissolved oxygen in shaft waters (Chen et al. 1999). While from a modelling perspective the buffering capacity of the mine was generally satisfied by calcite dissolution this is somewhat contradictory to the suggestion made by Younger (2004) that UK coal measures are generally lacking in calcium carbonates and that Fe carbonates are likely to dominate mine buffering processes. Using PHREEQC geochemical modelling it was predicted that uncontrolled mine water discharge at the

sites would result in goethite precipitation rates of approximately 36 kg/day, sulphate concentrations would range between 170 and 800mg l⁻¹ and pH be depressed to 6.5 (Chen et al. 1999). These effects at such magnitude would be short lived however it is expected that Fe between 1.5 and 2 mg/l would persist for many decades (Chen et al. 1999), consistent with the time evolution of discharge waters.

2.11 Mine water classification methods

Mine water is essentially groundwater with significantly altered chemistry due to the increased availability of oxygen for the dissolution of aquifer minerals. There are a number of conventions for the graphical representation and classification of groundwater chemistry including the bar, circular, radial, Stiff and Piper diagrams (Freeze and Cherry 1979, Appelo & Postma 2005). However, the Piper diagram (or Piper Plot) and the associated classification of groundwater *hydrochemical facies* is the most commonly used and universally recognised in the field of hydrogeology. In the last 20 years a number of specific mine water classification schemes have been developed and presented in the literature.

2.11.1 Acidity

The acidity of mine water is an important chemical parameter often used in mine water classification as it allows insight into the chemical evolutionary history of mine water and the potential hazard associated with discharge to the wider water environment. pH and acidity in the context of mine waters are two differing chemical terms. Younger (1995) described acidity as *‘the capacity of a solution to neutralize a strong base (e.g. 0.1 N NaOH) to a specified end-point (usually pH 8.3). Acidity thus defined is a reflection not only of hydrogen ion activity (proton acidity), which is explicitly given by the pH, but also of the ‘mineral acidity’ arising from the capacity of metals such as iron, manganese and aluminium to undergo hydrolysis reactions that release protons.* Often mine water acidity is not calculated via titration in the field, in this case acidity can be approximated with equation 9, below, originally presented by Hedin et al. (1994).

$$\text{Acidity}_{\text{Calc}} = 50[2\text{Fe}^{2+}/56 + 3\text{Fe}^{3+}/56 + 3\text{Al}/27 + 2\text{Mn}/55 + 1000(10^{-\text{pH}})] \quad (9)$$

This equation estimates acidity using the mine water pH and the concentrations of Fe, Al and Mn, which are generally the main metals which contribute to 'mineral acidity' in mine wasters. Acidities calculated in this manner have been shown to correlate closely with corresponding titrated acidities, with values differing by less than 10% (Hedin et al. 1994). This equation is likely only to be useful for minewaters derived principally from pyrite oxidation.

2.11.2 Piper plot

The Piper Plot represents the 8 major ions (SO_4^{2-} , Cl^- , HCO_3^- , CO_3^{2-} , Na^+ , Ca^{2+} , K^+ and Mg^{2+}), so called because they generally account for approximately 90% of the dissolved solids in groundwater (Fetter 1994), on a single diagram. This is achieved by representing the composition of anions and cations as a point on two triangular plots, the compositions are then projected on to a central diamond to plot as a single point. A major advantage of the Piper diagram, compared to less commonly used plots such as the Stiff, is that a large number of groundwaters with different chemical compositions can be represented and easily compared. Also, mixing of waters with different chemical compositions can be easily recognised by the relative position of end member and mix chemistry compositions. The Piper is often used to classify the hydrochemical facies of a groundwater with the dominant cation and anion species giving a double barrelled chemical facies name e.g. calcium-sulphate type or Ca-SO_4 . This is often a useful indication of groundwater source as different aquifer types have different hydrochemical facies associations. For example limestone aquifers which are dominated by carbonate minerals, calcite and dolomite, generally show calcium-bicarbonate, Ca-HCO_3 , or magnesium-bicarbonate, Mg-HCO_3 , groundwaters.

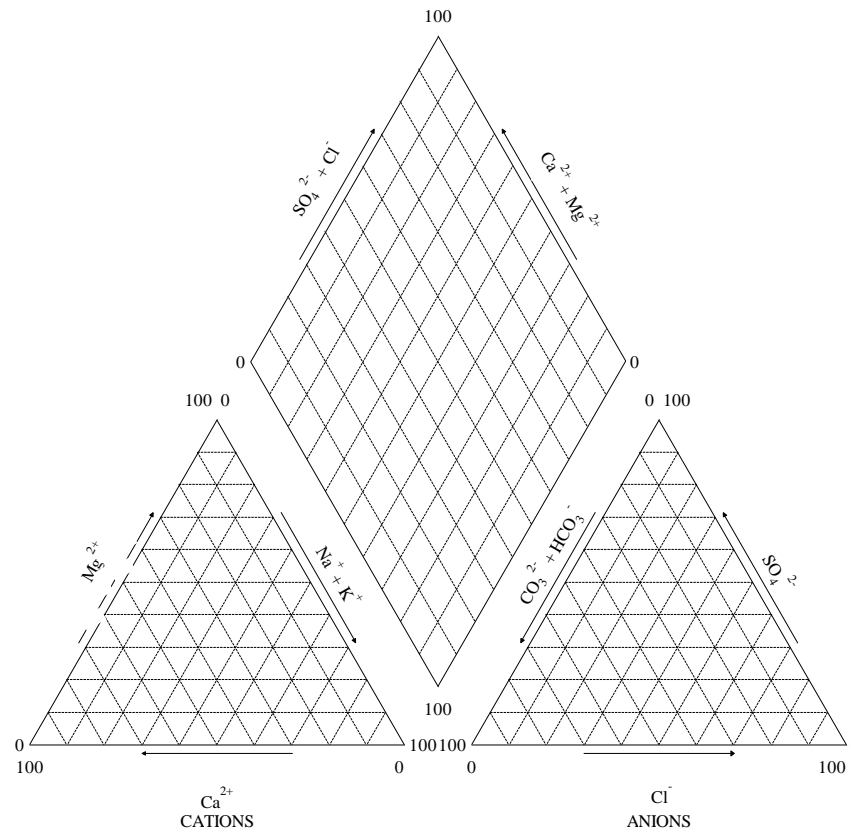


Figure 2.3- Example of the Piper Diagram (Created using USGS software GW Chart). The cations, as meq/l, are plotted on the left triangle, the anions are plotted on the right. The position of each is then projected on to the upper diamond shape.

While the Piper is widely used in the field of hydrogeology its usefulness in mine water hydrogeology is limited principally because it neglects iron and other dissolved metals which can be present at ‘major ion’ concentrations (Younger 1995). It is also difficult to represent pH or electrical conductivity on the piper, although this can be achieved by graduating the size of the point or symbol used to represent the chemistry.

A number of classification schemes have been developed exclusively for mine water classification these include; Glover (1975), which classifies waters by pH, Fe concentration and precipitate formation, US Bureau of Mines (by Hedin et al (1994) which classifies waters as either Net Alkaline or Net Acidic and Younger (1995) which classifies waters by percentage net alkalinity vs. sulphate dominance. The later of these is the most commonly used, principally because the classification gives an indication of pollution potential of a mine water, its source and potential remediation

options. Younger (1995) provides a more detailed explanation of the Glover (1975) and Hedin et al (1994) classification schemes which have not been specifically used in this study.

2.11.3 pH-Fe plot

The pH-Fe graph displays mine water pH on the X axis and Fe content on the Y axis; the resulting graph while simplistic in its classification is useful as a preliminary screening tool, particularly where data is limited.

2.11.4 Alk/Acid vs. SO_4^{2-} dominance

This plot originally proposed by Younger (1995) - uses a simple XY diagram with percentage alkalinity of alkalinity + acidity, as CaCO_3 , on the y-axis and $\Sigma(\text{SO}_4^{2-} + \text{Cl}^-)$ meq/l on the x axis (Figure 2.4). This classification is useful and so widely adopted because the XY parameters are directly related to the reactions which are generally of principal control on mine water evolution i.e. sulphide oxidation and carbonate buffering.

Mine waters which are sulphate dominant are heavily influence by pyrite oxidation and generally show higher Fe and other dissolved metal concentrations. An excess of alkalinity is indicative of carbonate buffering processes which increase alkalinity concentrations and water pH. In general, this reduces the mobility of dissolved metal species which are heavily pH dependent; however, mine waters with high alkalinity values may still contain considerably elevated metal concentrations. The hazard or 'pollution potential', as shown in Younger (1995), of a mine water increases towards the sulphate dominant region to the left of the diagram.

This scheme allows for the identification of pumped mine waters which plot in the top right of the diagram (being Cl^- dominant and net alkaline) as the action of pumping draws deeper and more saline groundwaters in to the mine complex. Furthermore, Younger (1995) indicates that the diagram maybe used to identify and track the chemical changes associated with mine water remediation such as, alkalinity increase, mineral acidity and sulphate reduction (see Chapter 5).

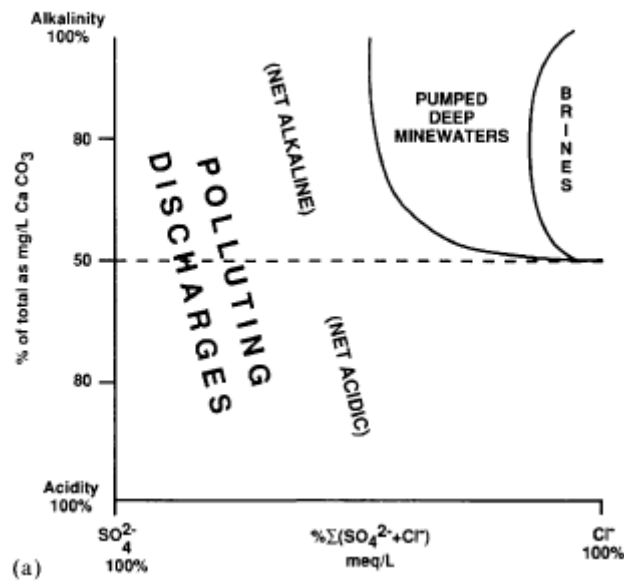


Figure 2.4- The alkalinity/acidity vs sulphate dominance plot as produced by Younger 1995. As indicated on the diagram the plotting position of a mine water indicates the possible source with the most polluting discharges plotting to the left and saline pumped waters plotting to the top right. Mine waters rarely plot in the bottom right of the diagram.

2.11.5 Net alkalinity modification

Rees et al. (2002) modified the Younger (1995) scheme to express alkalinity, on the X-axis, as absolute net alkalinity (i.e. alkalinity minus acidity). This modification allows for the differentiation of mine waters with different levels of acidity but zero alkalinity due to low $\text{pH} < 5$. Crucially, low pH discharge waters with different metal or ‘mineral acidity’ loads can be identified because acidity values are plotted as negative alkalinities. This splits the sulphate dominant higher pollution potential region to the left of the diagram into mine waters which are either net acidic or net alkaline. In general, the acidic and sulphate dominant waters are more polluting than the alkaline and sulphate dominant waters. However, net alkaline waters can still contain elevated metal concentrations as mineral acidity is balanced by an excess of alkalinity when carbonate buffering maintains near neutral pH, this is often the case in flooded mines where the scope for the generation of alkalinity exceeds that of acidity generation following groundwater rebound.

2.11.6 Hazard classification

Gray (1996) proposed an Acid Mine Drainage Index (AMDI), for the assessment of mine water hazard which assigns scores based on the concentration of seven chemical parameters (pH, SO_4^{2-} , Fe, Zn, Al, Cu and Cd) commonly found in mine waters. The assigned scores are then combined to produce an overall mine water value- the AMDI. Kuma et al (2011) suggested that using only 5 potentially eco-toxic metal species may underestimate the potential impact of mine waters which contain concentrations of metals other than those included in the AMDI method. Therefore, a modification was proposed by Kuma et al (2011) to incorporate a more extensive list of 20 potentially eco-toxic metals whilst still retaining seven chemical parameters to produce a Modified Acid Mine Drainage Index (MAMDI) value. This is achieved by grouping 20 metals into 4 groups based on relative toxicity, with each group being ranked based on the highest concentration of the metal within the group (Table 2.5). This has the advantage of incorporating contaminants into the ranking which would have otherwise been over looked. For example MAMDI allows the inclusion of Ni, which is a common contaminant in Scottish coal mine waters (Younger & Sapsford 2004) and would not be taken into account using the AMDI.

The AMDI and MAMDI schemes differ from the mine water chemistry classification schemes described above because they quantitatively assess the severity of impact associated with mine water discharge as apposed to assessing chemical, mineralogical, microbial processes.

Score	pH	SO ₄	Fe	Group 1 (Cu, Zn)	Group 2 (Al, Ag, Ba, Mn)	Group 3 (Pb, As, Se, CN, Cr, Mo, Ni, Sb, U)	Group 4 (Be, Cd, Hg, Tl)
25		<250					
24		250-299					
23		300-349					
22		350-449					
21		450-549					
20	>6.5	550-649					
19	6.2-6.4	650-799					
18	5.9-6.1	800-949					
17	5.6-5.8	950-1099					
16	5.2-5.5	1100-1399					
15	4.9-5.1	1400-1699	<1.0				
14	4.5-4.8	1700-1999	1.0-4.9				
13	4.1-4.4	2000-2499	5.0-9.9				
12	3.9-4.0	2500-2999	10-24				
11	3.7-3.8	3000-3999	25-49				
10	3.5-3.6	4000-4999	50-99	<1.0	<0.10	<0.01	<0.001
9	3.3-3.4	5000-6499	100-199	1.0-4.9	0.1-0.49	0.01-0.049	0.001-0.004
8	3.1-3.2	6500-7999	200-349	5.0-9.9	0.5-0.99	0.05-0.099	0.005-0.009
7	2.9-3.0	8000-9999	350-499	10-24	1.0-2.4	0.1-0.24	0.01-0.024
6	2.7-2.8	10000-11999	500-749	25-49	2.5-4.9	0.25-0.49	0.025-0.049
5	2.5-2.6	12000-13999	750-999	50-99	5.0-9.9	0.5-0.99	0.05-0.099
4	2.3-2.4	14000-15999	1000-1399	100-299	10-29.9	1.0-2.99	0.1-0.29
3	2.1-2.2	16000-17999	1400-1799	300-699	30-69.9	3.0-6.99	0.3-0.69
2	1.8-2.0	18000-20999	1800-2399	700-1199	70-119.9	7.0-11.9	0.7-1.19
1	1.5-1.7	21000-24999	2400-2999	1200-1999	120-199.9	12.0-19.9	1.20-1.99
0	<1.4	>25000	>3000	>2000	>200	>20.0	>2.0

Table 2.5 - Modified water quality scores for mine water discharge and contaminated surface water and groundwater for the calculation of MAMDI values. Table extracted from Kuma et al (2011). All contaminant concentrations in mgL⁻¹.

2.12 Mine water treatment

The processes of mining and the resulting chemical, mineralogical, bacterial and physical processes of contaminant mobilisation, outlined above, present significant environmental and water quality issues in heavily mined areas. In response to this, particularly over the last few decades, technologies have been developed to prevent, reduce and limit the impacts of mine related contaminants via the development of mine water treatment technologies. These can be broadly split into two groups 1) active treatment which generally requires pumping, chemical dosing and the continual exertion of energy (e.g. Glover 1983) or 2) passive treatment which uses an engineering solution to treat mine waters at source using naturally available energy sources with infrequent maintenance (PIRAMID 2003).

The preferred option for mine water treatment from abandoned coal mines in the UK is passive treatment. In general ‘Active plant is used as a short term solution or when the required land area for a passive scheme is not available’ (The Coal Authority

Website). In response to the needs of the UK and other European countries the research project PIRAMID (Passive In-Situ Remediation of Acidic Mine/Industrial Drainage) was set up and design guidelines (PIRAMID 2003) were published. Other key works in this area include those by Hedin et al. (1994) which details works undertaken to move from active treatment of mine waters in the US to passive treatment, as well as a number of modern novel approaches involving permeable reactive barriers (Jarvis et al. 2006). Outlined below is a brief review of the main passive treatment methods used to reduce the impacts of mine water discharge. For a more detailed overview of the complex geochemistry operating with the various treatment options the aforementioned studies should be consulted.

Aeration and Settlement

Where the dissolved oxygen content of mine waters is low there is limited scope for the oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}). This is significant because many treatment options utilise the precipitation of Fe^{3+} from solution to the solid iron hydroxide $\text{Fe}(\text{OH})_3$ to reduce dissolved Fe concentrations (e.g. Hedin et al, 1994a). Therefore, increasing dissolved oxygen concentrations can afford reductions in dissolved Fe concentrations; this can be achieved simply by a series of stepped cascades which allows aeration of the cascading mine waters (Younger et al. 2002). Other processes for aeration include in-line venturi aeration where a small pipe, open to the atmosphere at one end is placed into a closed flow of mine water allow significant oxidation of iron (Ackman & Place 1987, Ackman 2000, PIRAMID 2003) and mechanical aeration. However, mechanical aeration generally requires the exertion of energy and therefore can not be strictly classified as 'passive'. For mine waters containing high concentrations of Fe cascades will often be used prior to discharge into a settlement lagoon. In settlement lagoons used by the Coal Authority in the UK up to 70% of the dissolved Fe has been shown to be removed (PIRAMID 2003). Open lagoon, compared to wetland treatment, have the advantage of being easier to clear of settled solid Fe for off site disposal. Aeration and settlement systems are best suited to alkaline mine waters because the Fe oxidation reaction is sensitive to reductions in pH (PIRAMID 2003).

Aerobic Wetlands

Aerobic wetlands are constructed such that mine waters are passed through a planted reed bed area which slows the flow of water, increase residence time and aerates the water with the use of vegetation (Batty and Younger 2002, Zipper et al 2011). Within the wetland a number of processes as defined by in the PIRAMID (2003) guidelines may occur to reduce Fe and other metals concentrations including sedimentation of suspended flocs, filtration of flocs by stems of plants, adsorption of aqueous metal species, precipitation of hydroxides on plant stems and the wetland sediment surface, and direct plant uptake. In general waters are passed over the wetland at depth of up to 0.5m (Hedin et al. 1994a, Younger 1995). Due to the release of proton acidity, H^+ , during Fe precipitation, reductions in pH occurs, because of this aerobic wetlands are best suited to alkaline mine waters with modest (around 5mg/l) Fe concentrations. However, in some cases aerobic wetlands have been used effectively with much higher Fe concentrations (Watzlaf et al. 2003).

Compost/Anaerobic Wetlands

In appearance anaerobic wetlands are similar to aerobic wetlands, having reed vegetation and the reduced flow of shallow influence waters at surface, however, they also use an organic substrate material, such as compost mixed or layered with limestone chips to promote bacterial processes which consume acidity, generate alkalinity and removed metals (Hedin et al. 1994, Walton Day 1999, PIRAMID 2003). Such processes are most effective for the treatment of acidic mine waters. Microbes within the substrate use sulphate from the influent waters and organics from the substrate via sulphate reduction reactions to bind metals in an insoluble monosulphide. Dissolved aluminium is also effectively treated via the formation of $Al(OH)_3$ deposits within the substrate due to the elevation of pH from sulphate reduction and limestone dissolution (PIRAMID 2003). As effluent waters have low dissolved oxygen concentrations, anaerobic wetlands are often discharged into aerobic wetlands to increase oxygen concentrations and promote the removal to the remaining dissolved metal concentration as hydroxides (PIRAMID 2003).

Anoxic limestone Drains (ALDs) and Oxic limestone Drains (OLDs)

ALDs and OLDs increase bicarbonate alkalinity by passing waters through a buried trench containing a limestone substrate; carbonate buffering increase alkalinity and raises the pH of waters (Hedin et al 1994a, 1994b, Younger 1995, PIRAMID 2003 Zipper et al 2011). The optimum limestones for use in such systems must contain high (>80%) CaCO_3 content, as such dolomite is rarely used (PIRAMID 2003). ALDs must be kept anoxic to prevent armouring of the limestone by iron hydroxides which renders the trench useless. OLDs are identical to ALDs but are able to accept oxygenated waters; armouring of the limestone is prevented/reduced by keeping the flow rate high enough to keep solids suspended for settlement in an associated lagoon or wetland (Ziemkiewicz et al. 1997, Cravotta & Trahan 1999).

Reducing (Successive) and Alkalinity Producing Systems (RAPS/SAPS)-

A RAPS is effectively an ALD combined with a reducing compost bed, they are designed to treat acidic mine waters with elevated concentrations of dissolved oxygen, ferric iron and / or aluminium. The system works by removing dissolved oxygen from waters as they pass through the compost and reducing Fe^{3+} to Fe^{2+} ; alkalinity generation then occurs in the limestone which is beneath the compost layer (Kepler & McCleary 1994, PIRAMID 2003). These systems were originally termed Successive Alkalinity Producing Systems by Kepler & McCleary (1994) as a series of these units could be installed in a successive manner; however the PIRAMID (2003) guidelines indicate that in most cases only a single unit is required followed by an aerobic wetland, hence the RAPS description is considered more appropriate. RAPS are the favoured systems for the treatment of acidic waters in the UK (PIRAMID 2003). Systems are generally not designed to promote sulphate reduction in the compost layer, however this has been found to be a significant beneficial benefit in some cases. The principal limiting factor in the application of RAPS is the requirement of significant relief on site to provide the system with enough head space.

2.13 Environmental legislation

Several pieces of environmental legislation relate specifically to the environmental impact of mining or more generally cover the management of impacts of anthropogenic activity on the water environment. These are outlined below.

The Water Framework Directive(WFD)- was established by Directive 2000/60/EC by the European Parliament in October 2000 and was implemented in December 2003. The principal aim of the WFD is to achieve good chemical or ecological status for all groundwaters and surface waters. A key aspect of the legislation is that water is considered on a river catchment scale, independent of political or anthropogenic boundaries. This piece of legislation is an overarching act for maintenance of the water environment. All EU member states are required to adopt the legislation. In Scotland the legislation was disseminated into Scottish law by the Water Environment and Water Service Act 2003. The directive makes little specific reference to mining, however, as it is well understood that mining prevents the achievement of ‘good’ surface water and groundwater the directive therefore requires that the impacts of mining be managed. And where possible the impacts reversed. There is some debate as to whether the directive applies to mine waste (Kramer 1999, Kroll et al. 2002)

The Mine Waste Directive- was established by EU Directive 2006/21/EC. It requires that waste from extractive and mine industries are dealt with in a manner that does not result in impacts on human health or the environment. This legislation is specifically designed to deal with waste from active mining industries, however, specific measures are outlined associated with abandoned mine wastes from historic sites.

The Groundwater Directive and Groundwater Daughter Directive- The groundwater directives aim to protect groundwater from pollution by prevention of discharge of harmful substances. These are divided into substances which are hazardous and non-hazardous (previously List I and List II). The determination as to

which category a substance will fall is based principally on 1) their toxicology, 2) persistence in the environment and 3) bio-accumulation potential.

Hazardous substances- are those which are most hazardous to the environment and generally being toxic, persistent and bio-accumulative. They include pesticides, solvents, hydrocarbons, mercury and cadmium. The discharge of hazardous substances to the environment should be prevented in accordance with the directives. Hazardous substances in mine water are rare; however, elevated concentrations of cadmium, Cd, and mercury, Hg, are occasionally recorded.

Non-hazardous substances- generally do not display all three of the determination criteria mentioned above but may fall into one or possibly two of the categories. Ultimately the determination of the hazardous and non-hazardous list is the decision of a national working group based upon the available evidence for each substance. In mine waters non-hazardous substances include elevated concentrations of sulphate, iron and other metals. The discharge of these substances is permitted but only where the resulting increases in concentrations does not cause pollution which may have adverse impact to a receptor. Therefore, while the discharge of Fe to groundwater in itself is permissible every action should be taken to prevent the pollution of a water body if that pollution will impact ecology or human health.

Chapter 3

Scottish Oil Shale: the environmental legacy

3.0 Introduction

Oil shale deposits, estimated at 11.5 trillion tonnes, are found around the globe in countries including France, Estonia, America, Canada, China and Scotland (EASAC 2007). UK Oil Shale*, estimated at 3500 million barrels, was the first oil shale reserve in the world to be exploited on a commercial scale for oil production in the Scottish Shale Oil Industry. As a result for a short period in the late 19th century Scotland became the world's largest oil producing nation long before any oil was discovered in the North Sea (Hallett et al. 1985). The oil shale source rock for the industry was organic rich Carboniferous aged shale formed in a large restricted anoxic lagoon related to a large late Devonian to Carboniferous aged graben basin in which all of the sedimentary rocks of the Midland Valley were deposited (Browne et al. 1999).

The organic content of the shale was exploited using an industrial scale processing method developed by the Glaswegian inventor James 'Paraffin' Young in 1850. Oil and other industrial products were produced by heating the rock in a variety of retort designs at large processing sites which were located across West Lothian. The industry lasted for over a century from 1851 to 1962 reaching peak output in 1913. The industry, as well as providing social and economic benefit to the region and the country, pioneered oil refinery methods and developed expertise which placed Scotland in an experienced and knowledgeable position when North Sea Oil was discovered. Unfortunately, the industry also had significant historic environmental and water quality impacts, some of which persist to the modern day. Mining and processing of the oil shale led to water quality issues which were only worsened with

***Oil Shale** is the organic rich shale which was processed to produce **Shale Oil** which is similar to naturally occurring crude oil

mine abandonment due to the uncontrolled discharge of mine waters at surface. This chapter introduces the geology of oil shale, the history of the shale oil industry and examines the modern environmental impact potential of this hugely significant and underappreciated industry.

3.1 Geology

The Scottish oil shales are found as approximately twenty distinct seams of various thicknesses and quality in the West Lothian Oil Shale Formation (WLO), historically referred to as the Oil Shale Group (Carruthers 1927, Louw and Addison 1985, Browne et al 1999). The West Lothian Oil Shale Formation has a maximum thickness of up to 1200m (Figure 3.2) and is a cyclic sequence dominated by pale sandstones with oil shales, siltstones, mudstones, subordinate limestone and coals (Browne et al 1999). Raw oil shale, as it is found in the seam, is a brown to black, fine grained and minutely laminated clay shale containing a significant but variable organic content. It is resistant to weathering and was recognised by the oil shale miner by a distinct brown streak and its ability to be cut by a knife (Bailey 1927, Sneddon et al. 1938, Louw and Addison 1985). Oil shales like coals were exploited due to their organic content; however, they have a greater mineral content, up to 60%, compared to less than 20% for most coals (Cadell 1925).

The sediments and oil shales of the West Lothian Oil Shale Formation were deposited in a large tropical lagoon part of the Central Scotland rift valley which is bound by the Highland Boundary and Southern Upland Faults (Cameron & Stephenson 1985, Harvie 2010). A number of different sediments were formed in the lagoon, referred to as Lake Cadell, associated with variable sea level. Limestones formed in shallow waters from coral reefs and coals were formed from primitive plants and swamp environments on the edges of the lagoon. The oil shales were formed in the deeper areas from the deposition of fine grained sediments and plant debris (Cadell 1925), including a significant proportion of pollen and plant spores. Oil shale deposition occurred when the lagoon was stagnant, stratified and anoxic at depth which prevented the breakdown of organic matter (Follows & Tyson 1998). Pyrite, which is found as a subordinate mineral phase in the shale, confirms the

reducing conditions of the depositional environment (Moore 1968). Total organic carbon content (TOC) is in the order of 10-12% for the organic rich shales, classified as Type II to Type I amorphous kerogen (Follows & Tyson 1998). Organic matter in the shales was washed in from the flanks of the lagoon where peats and coal formed in forested areas. The matter is principally algal, fungal, bacterial and animal material with microspores and resins (Moore 1968). It is this organic content which made the oil shale of industrial use via the destructive distillation of the rock to form a type of crude oil.

The minute lamination of the shale, which, until burned, is only recognisable under the microscope, is interpreted as being the result of seasonal or water level changes in the lagoon (Moore 1968). The laminations represent different layers of organic rich and mineral rich materials deposited and also indicate the lagoon lacked any significant turbidity or bottom currents. The majority of oil shale deposits are associated with 'blaes', a historic term used to describe the hardened clay and mudstone bands which under-lie and over-lie most of the shale but, unlike the oil shale, are generally lacking in economically viable organic content (Cadell 1925, Carruthers 1927, Moore 1968). The sandstone and more arenaceous sediments which are interbedded with the twenty distinct oil shale horizons in the formation represent the inundation of the lagoonal environment with more distal sediments washed down from the surrounding terrestrial environments (Figure 3.1).

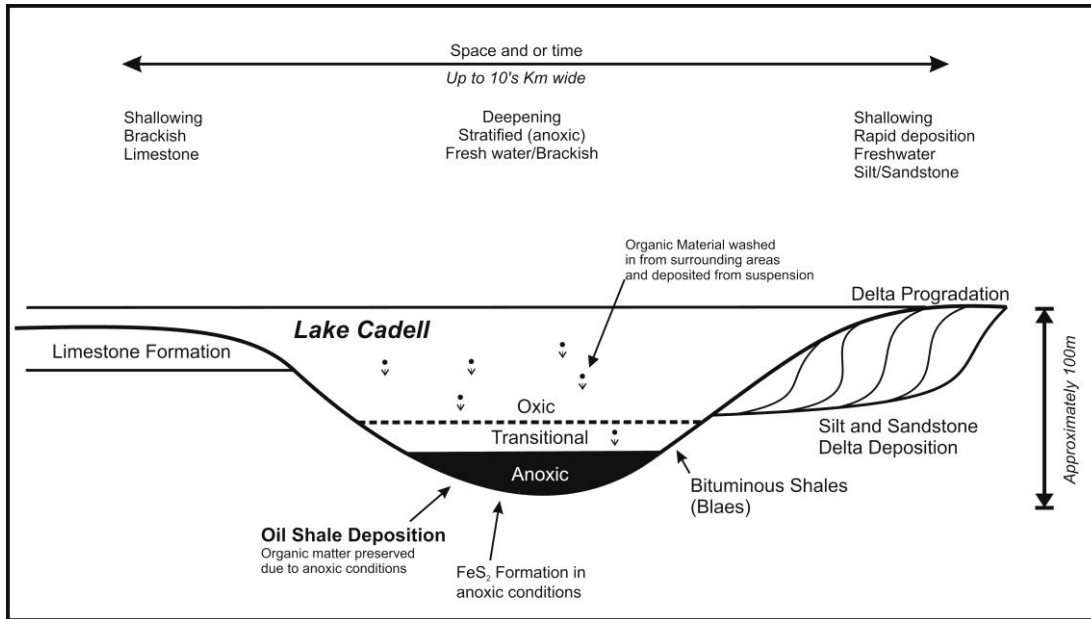


Figure 3.1 - Depositional Environment of the West Lothian Oil Shale Formation, after Follows and Tyson (1998). The diagram indicates how anoxic conditions in the base of the lake aided the preservation of organic matter but also the formation of pyrite in reducing conditions. The Sandstone/siltstone and limestone depositional environments at lake edges are also shown.

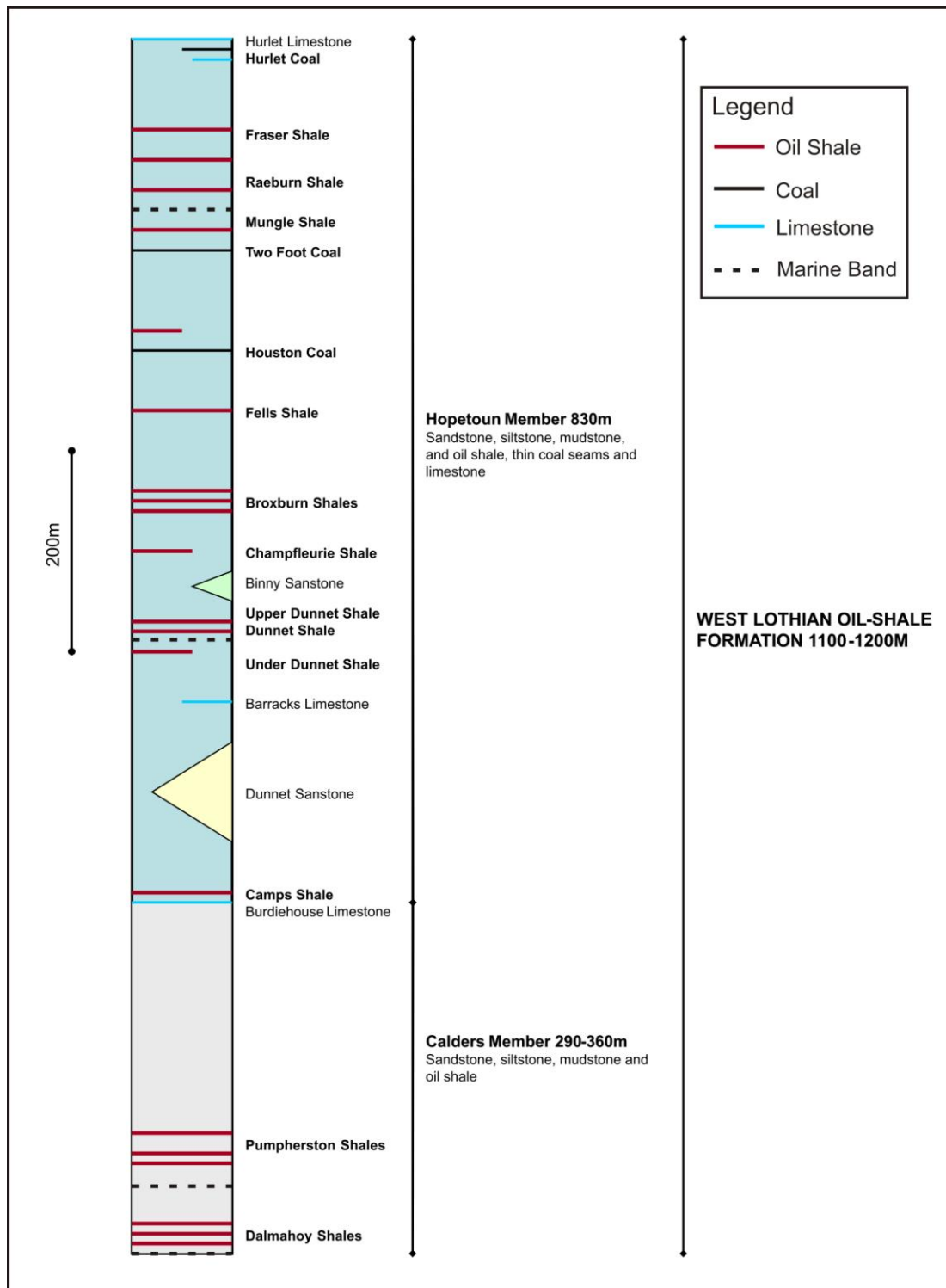


Figure 3.2 - Generalised Vertical Section of the West Lothian Oil Shale Formation. British Geological Survey © NERC. The section shows the separation in the two members of the West Lothian Oil Shale Formation, the red lines indicate the position of oil shales, the black lines indicate the position of the coals.

3.2 Mineralogy

The term 'oil shale' only has a loose definition based on the identification of a rock with a significant proportion of organic content, which may be extracted by the application of heat (Brendow 2003). The mineralogical and organic content of oil shales can vary significantly depending on the reserve in question, for example Green River Oil Shale in America has a carbonate mineral content of up to 40% (Chilingarian & Yen 1976), whereas Scottish Oil Shales generally have a lower carbonate content but a dominant clay mineral content, making them a true shale. Table 3.1 contains mineralogical data from x-ray diffraction (XRD) and infrared spectroscopy (IR) analysis on samples from a number of oil shale seams in the West Lothian Oil Shale formation, originally presented by Louw & Addison (1985). The analysis indicates that the oil shales consist predominantly of quartz, kaolinite, mica and occasionally contain carbonates where the shale has a larger limestone component (ie. marl). Lesser fractions of feldspars, siderite and pyrite are also contained in the shale.

	1.Pumphreston	2. Camps	3. Dalarnhoy	4. Under Dunnet	5. Dunnet	6. Broxburn	7. Raeburn	8. Broxburn	9. Broxburn	10. Broxburn	11. Broxburn Mart
Quartz	8.4	8.3	14	16.4	12.5	14.3	8.5	7.7	14	14	12
Kaolinite IR 380oC Ash	40	15	22	25	32	31	34	10	17	13	1
Mica IR 700oC Ash	20	3	20	23	24	23	19	33	28	37	n.d.
Calcite	n.d.	22	tr	tr	tr	n.d.	tr	tr	n.d.	tr	23
Dolomite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4
Siderite	2	2	tr	tr	tr	tr	n.d.	tr	5	6	n.d.
Plagioclase	n.d.	tr	tr	1	1	tr	n.d.	tr	1.5	tr	7
Orthoclase	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Analcime	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1
Other Minerals	1% Py	1% Py	tr Py	tr Py	tr Py	tr Py	3% Py	1% Py, tr Gy	tr Py	tr Py	2% Py

Table 3.1 - XRD Analysis of Oil Shale Seams in West Lothian, Py=pyrite, Gy= Gypsum (Louw and Addison 1985). The table shows mineralogical analysis results from 11 samples recovered from some of the main worked oil shale seams in West Lothian.

Coal sulphur content is well studied because it has significant implications for coal utilisation (Spears et al. 1999); this was less significant historically, however, today sulphur content is often used as an indication of the potential environmental impact of mining (e.g. Younger & Adams 1999, Younger & Sapsford 2004). Table 3.2 contains the sulphur content of some commonly worked oil shale seams in the West Lothian Oil Shale Formation, presented in Bailey (1927). The relationship between

sulphur content, pyrite and mine water chemistry for coal mines is well established, its considered that in general these relationships may be similar for oil shale. In coals, sulphur is predominantly contained in organic material when the seam contains below 0.5% sulphur. Above this, additional sulphur is contained within pyrite and above 1% S approximately 50% of the sulphur in a coal, is contained in pyrite (Younger 2002, Younger & Sapsford 2004). Therefore, the higher the sulphur content, the higher the pyrite content.

Oil Shale Horizon	Sulphur Content %
Fells Shale	1.01
Broxburn Shale- No.1	1.13
Broxburn Shale- No.2	1.25
Broxburn Shale- No.3	1.02
Lower Dunnet Shale	1.27
Camps Shale	2.04
Pumpherstons Shale No.1	0.44
Pumpherstons Shale No.2	0.49
Pumpherstons Shale No.3	1.46
Pumpherstons Shale No.4	1.29
Pumpherstons Shale No.5	1.45

Table 3.2 - Sulphur content of some commonly worked Oil Shale seams in the West Lothian Oil Shale Formation (Bailey 1927).

3.3 Shale oil industry

3.3.1 Historical overview

The oil shale industry started with the invention of an industrial scale hydrocarbon extraction method, developed and patented by James Young in 1850. The patent concerned the extraction of hydrocarbons from the Boghead cannel coals which were found close to Bathgate, West Lothian. The cannel coal deposits, originally targeted by Young and processed in the Bathgate facility he built and opened in 1851, yielded high quantities of oils. However, the availability of cannel coals was extremely limited to an area of 2500 acres and, therefore, were exhausted within a decade (Hallett et al. 1985). Experiments on the Lothian Oil Shales revealed that they could also be used to produce hydrocarbons on exposure to heat (Redwood 1897). The oil shale in the West Lothian Oil Shale Formation represented a much more significant potential resource than the cannel coal; however, they did tend to give a lower hydrocarbon yield (30-40 gallons per ton) than the cannel coals (85-128 gallons per ton) (Redwood 1897, Louw & Addison 1985). Young began processing the shales in his newly built Addiewell processing facility in 1866, however, this activity and the potential profits did not go unnoticed and others began to mine and process the Lothian Oil Shale. Young having patented his extraction method enforced it in court several times with varying success. The size of the Addiewell works, producing a 3rd of the total output of the industry, became troublesome as other smaller works could adapt more quickly to advances in retort design and increase oil and by product yields (Redwood 1897). Ultimately Young's patent expired and wasn't renewed; by 1863 over 50 different oil shale works were processing oil shale in West Lothian (Redwood 1897).

By 1916 the industry employed over 5000 miners and processed over 3 million tons of oil shale per year. Foreign competition from 'free running' oil resulted in the general decline in Scottish oil production, however, the UK government offered significant tax relief allowing the industry to continue (Hallett 1985). This proved very beneficial in both the First and Second World War as it enabled a secure homeland source of hydrocarbons. After approximately 100 years the Scottish Oil

Shale industry came to a close with the decommissioning of the Westwood oil shale works in 1962.

3.3.2 Mining

Over the lifetime of the oil shale industry inclined subsurface mines were the most common types of mine used to extract oil shale (Figure 3.5), although opencast mining was also used in a number of areas, particularly at the earliest mines (Sneddon et al. 1938, Kerr 1994). The first recorded oil shale mine opened in Broxburn; mines quickly spread across the whole of the West Lothian Oil Shale Formation outcrop areas which ran from the shores of the Firth of Forth down to West Calder and Tarbrax. The depth of mining was relatively shallow, compared to coal mining in the Scottish Coal Measures to the west, with working depth sometimes less than 30m and in general less than 100m. However, some areas of deeper mining were undertaken particularly north west of Pumpherston and the Eliburn area north west of Livingston village (MacAdam et al 1992).

	Working Depth			N° Worked Mines	Worked Area (ha)
	Opencast	<30m	>30m		
Fraser Shale	NA	NA	NA	4	118
Raeburn Shale			✓	3	9
Grey Shale	NA	NA	NA	1	-
Fells Shale		✓	✓	27	787
Broxburn Shales	✓	✓	✓	59	1548
Chamfleurie Shale		✓	✓	1	52
Upper Dunnet Shale	✓	✓	✓	6	28
Dunnet Shale	✓	✓	✓	34	983
Under Dunnet Shale		✓	✓	9	87.5
Pumpherston Shale	NA	NA	NA	4	491

Table 3.3 - Oil Shale Seams, associated workings and depths in the West Lothian Oil Shale Formation (data compiled from Louw & Addison (1985) and MacAdam et al. (1992))

Mining was undertaken generally by ‘Longwall’ or ‘Stoop and Room’ methods with the latter becoming more popular as the industry progressed (Sneddon et al 1938, Kerr 1994). The total number of significantly worked mines in West Lothian, according to a gazette compiled by Scottish Oil Ltd (1947), was 162. A similar number, 156, is presented, sorted by worked seam, in Louw and Addison (1985). The

total area worked in the subsurface is estimated at over 4000ha. Table 3.3 indicates that the Broxburn seams were by far the most productive followed by the Dunnet and the Fells. These seam sets are the central three in the cyclic succession of the formation (Figure 3.2) and run in a north south band from West Calder to the shores of Blackness. Their arrangement is complicated by a series of faulted anticlines and synclines which cause them to outcrop in a series of curved almost of ring like arrangements around West Calder and Broxburn. The increased abundance of outcrop in these areas resulted in them being the most intensively mined in the region.

Total oil shale mined, based on figures by Bailey (1927) and Stewart (1966) is 163 million tonnes, however, production varies significantly over the lifetime of the industry, reaching a peak production of 3.28 million tonnes per year in 1913 and during the First World War (Figure 3.4). This was no coincidence as having a secure national supply of hydrocarbons was extremely important during the war time. The Shale Oil Industry was not confined to petroleum production and the industry produced or facilitated production of many other products in West Lothian including lubricating oils, solvents, paraffin wax, ammonium sulphate, sulphuric acid, gas, candles and paints (Hallet 1985, Harvie 2010). The industry could even be said to have indirectly lit the trenches of the First World War, WWI, as great quantities of Young's Paraffin Candles were sent to the front line (Figure 3.3). Following WWI the industry went into steady decline and the four main Shale Oil companies- Broxburn Oil, Oakbank Oil, Young's Paraffin Light and Mineral Oil and Pumpherston Oil merged to form Scottish Oil Ltd, in 1918 (Conacher 1938). The intention of this was presumably to reduce costs and increase productivity, however, production continued to decrease... *'..in June 1925, Sir John T. Cargill, the chairman, told the shareholders of Scottish Oils Ltd., that in spite of every economy, owing to low prices for the products, the distillation of the shale had ceased to yield a profit, and that the mines, which afforded the livelihood to 30,000 or 40,000 people, were being kept going mainly from patriotic motives.'* (Cadell 1925 p36.)



Figure 3.3- A photograph image of two gentlemen with Young's Paraffin Candles ready to be sent to the trenches of the First World War as indicated by the plack in the centre of the image (Reproduced with permission of the Almond Heritage Trust).

The Second World War resulted in a resurgence of production of oil shale mined to 1.78 million tonnes per year, however by this time the industry could be said to be in terminal decline (Figure 3.4). In 1962 the Westwood Works, close to West Calder and associated with the now protected Five Sisters Oil Shale Bing, was closed. The Westwood was modern and efficient compared to historic processing facilities, however, the cost and energy of mining and processing oil shale compared to that of foreign imports of oil ultimately made the industry economically unviable. The total output of the Scottish Oil Shale Industry is estimates at 75 million barrels (Hallett et al 1985). It is estimated approximately 1100 million barrels remain in the West Lothian Oil Shale field (Cameron & McAdam 1978).

One lasting legacy of the industry, other than the striking and obvious oil shale bings littered across West Lothian, is the knowledge and experience gained in refinery and large scale industrial processing of oils. This knowledge was put to good use in the formation of British Petroleum (BP) and with the discovery of North Sea Oil in 1969 (Hallett et al 1985) Scotland was in the unique position of already having over 100 years of experience in oil refinery and processing.

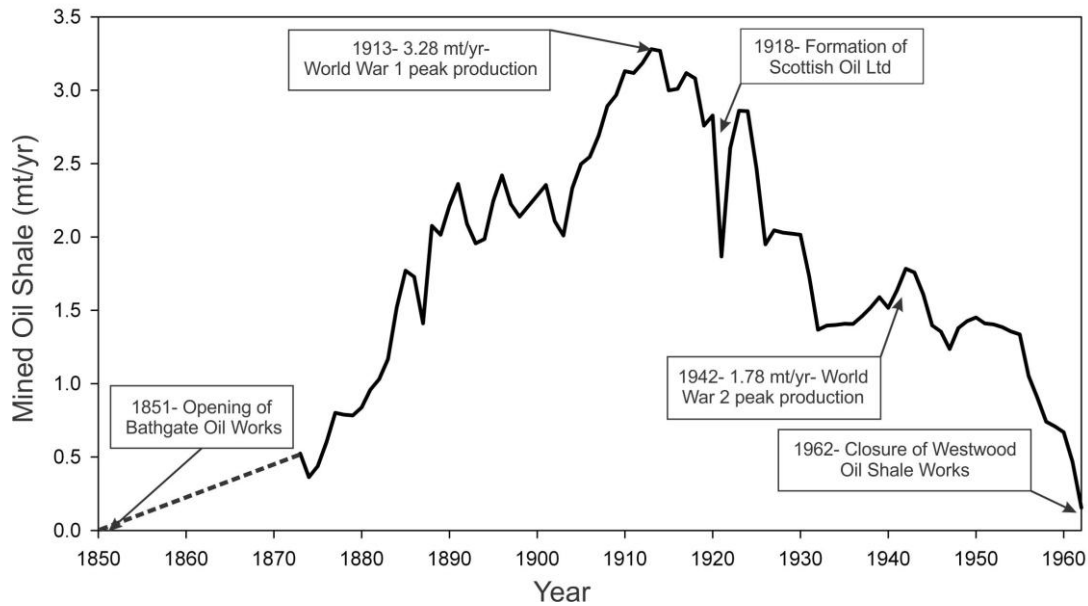


Figure 3.4 - Quantity of oil shale mined by the Oil Shale Industry in Scotland. The industry began with the opening of the Bathgate Oil works in 1851 and saw a steady increase in production until just prior to the First World War. The industry then went into decline before closing in 1962 (After Bailey 1927 and Stewart 1966)



Figure 3.5- Historic photograph showing an inclined entrance to an oil shale mine. The hutches used to transport the oil shale out of the mine can be seen on the right hand tracks. It is clear from the image that mine waste was piled up around the entrance to the mine. (Reproduced with permission of the Almond Heritage Trust)

3.3.3 Oil Shale Processing

Processing of oil shale, following exhumation from the mine, in its most simplistic form involved the application of heat within a sealed container, termed a retort, from which liquid and gas hydrocarbon products were syphoned. The way in which this was achieved changed over the lifetime of the industry with advances in technology leading to increased yields of oil and by-products as well as significant efficiency increases. The many different companies initially involved in the industry encouraged innovation as each tried to increase yields and minimise costs. Every potential variation in retort design cannot be easily described but the main types, as described by a number of studies (Redwood 1897, Bailey 1927, Stewart et al 1938, Louw & Addison 1985) are outlined in Table 3.4.

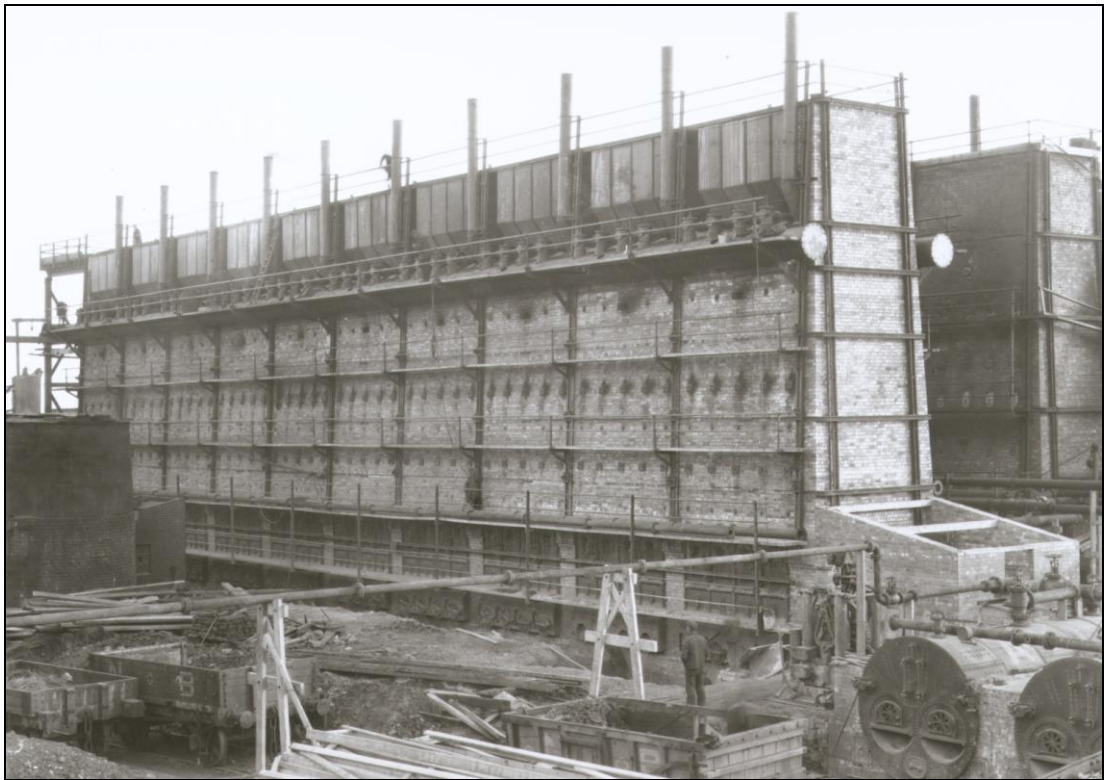


Figure 3.6 - A row of Pumpherston type oil shale retorts at a historic processing facility in West Lothian. Raw crushed oil shale was tipped into the top of the retort and gravity fed through the chambers inside where it was heated to remove hydrocarbons and other chemicals. The pipes on the outside were used to siphon the products off the retort. (Reproduced with permission of the Almond Heritage Trust)

Retort Type	Operational Period	Notes
Horizontal	1850-1880	<ul style="list-style-type: none"> • Horizontal D shaped Retort, originally for cannel coal also used for oil shale • Metal retort sealed with fireclay and heated by a coal furnace • Intermittently charged by shovel • Residence time 16-24 hours • Little to no temperature control, 'cracking' of product was common place • Typically associated with the Bathgate Chemical Works.
Lowe and Kirkham	1852- dependent on modification	<ul style="list-style-type: none"> • Vertical Retort • 3 cast iron cylinders in a coal fed fire chamber • Several modifications including elliptical cross section. This allowed for better heat distribution and reduced 'cracking' of heavier oils.
Kirk's		<ul style="list-style-type: none"> • Vertical, elliptical and tapered with larger base • Better through flow of shale, no need for mechanical aid • Lesser yields of some products compared to horizontal due to light end oils being converted to gaseous products • First mention of steam injection for uniform heat distribution
Henderson	Patented 1873 used until 1892	<ul style="list-style-type: none"> • Spent shale's remaining carbon (12%) was burned in the fire chamber. 50% reduction in fuel used to heat the retorts. • Oil product removed lower in the retort • Steam injection increased oil yield
Beilby	1881-1883	<ul style="list-style-type: none"> • First 'two stage' design. Upper cast iron, lower fireclay • Maximised oil and ammonia extraction yields with minimal oil loss from 'cracking' • Spent shale is not burnt, gas product is used to heat the retort • Design ultimately failed due to strain of temperature difference causing the fireclay sections to crack.
Pentland	1882	<ul style="list-style-type: none"> • Vertical, two stage • Mass industrial design of 16 shale retorts in 2 ovens operated 24 hrs 7 days • Prolonged maintained temperature, minimal 'cracking', very good yields • Lower section reached upper limit of 750°C. • Heated by coal, and gas product
Pumpherson	1894-	<ul style="list-style-type: none"> • Vertical, two stage, circular x-section • Automated design, including shale being delivered by hoppers to the top of the retort, reduced labour cost and increased efficiency

		<ul style="list-style-type: none"> • Heated by coal, external gas and gas product • Steam injection • Later adapted for air injection
Broxburn	1889-1940	<ul style="list-style-type: none"> • As Pumpherston except square x-section
Young's	1913-1940ish	<ul style="list-style-type: none"> • Similar to Pumpherston and Broxburn but slightly smaller • Discharge of shale was from the side instead of base • Later adapted for air injection
Westwood	1939	<ul style="list-style-type: none"> • Similar to Pumpherston and Broxburn but maximised for efficiency • Air injection accurately controlled at various points. Massively reduced residence time and increased yield • Extremely efficient, following initial external heat source to begin retort process the retort would then run entirely off gas produced as part of the extraction process • Used at the last oil shale works, Westwood. Efficiency drive due to WWII.

Table 3.4 - Summary of the principal development in retort design in the Scottish Oil Shale Industry. The main retort types, the operational period of each and a description is provided. (Information from Redwood 1897, Bailey 1927, Stewart et al 1938, Louw & Addison 1985)

Table 3.4 indicates that the most significant advances associated with the oil shale retort designs involve 1) the development of a two stage process to maximise both oil and ammonium yields, 2) burning of residual carbon and gas to minimise the need for external heat sources, 3) steam injection for increased temperature distribution and control, and 4) air injection for increased yields and through flow of shale.

Early in the industry when retort technology consisted of horizontal or basic vertical retorts the temperature control would have been solely controlled by the retort operators' application of coal to the furnaces heating the retorts. This means that overheating and 'fusing' of the shale was common place, when this happened the whole process would have to be stopped and the fused shale removed. Evidence of this can be seen at many of the shale waste sites (Bings) across West Lothian where rock like fragments of fused oil shale can be found.

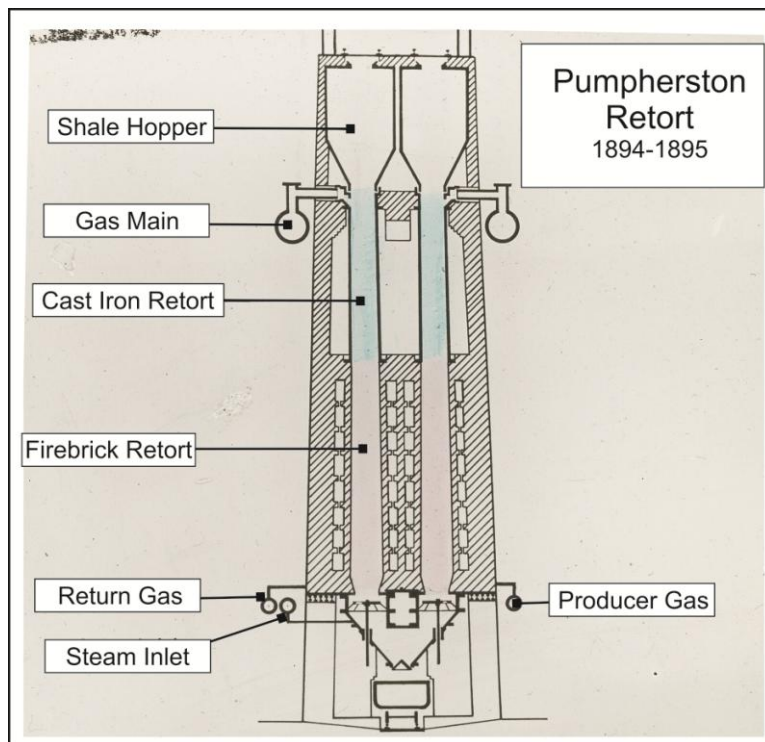


Figure 3.7 - Pumpherston Retort showing many of the principal features of retort technology. Raw oil shale is fed into the shale hopper and is gravity fed through the two separate retorts. Hydrocarbons are siphoned in the upper retort and ammonium and other accessory chemicals in the lower retort. The waste shale is then dropped into the hutch below and transported to a waste pile (Reproduced with permission of The Almond Valley Heritage Trust)

Redwood (1897) lists 117 oil works in Scotland, however not all of these were located in the Lothians or necessarily associated with the Oil Shale. Nevertheless, the scale of oil shale extraction and refinery compared to anything that had come before can only be described as colossal. Outlined in Table 3.5 is a select number of the main oil shale processing sites which operated in the Almond River Catchment, West Lothian. The location of the works relate to the numbered locations on Figure 3.9. Most sites would contain several ‘benches’ of retorts, therefore, many hundreds, possibly thousands, of retorts were operated over the lifetime of the industry. No physical remainders of the actual retort sites can be found in West Lothian today, but what remains is the huge volume of processed and unprocessed oil shale mine waste littered across the landscape.

Number	Name	Operational Period
1	Cobbinshaw South Oil Works	1870-1877
2	Cobbinshaw North Oil Works	1870-1875
3	Hartwood Paraffin Oil Works	1871-1873
4	Hermand Crude Oil Works	1867-1873
5	Hermand Shale Oil Works	1867-1875
6	Burngrange Shale Oil Works	1867-1868
7	Addiewell Chemical Works	1866-1958
8	Westwood Paraffin Works	1866-1871
9	Westwood Oil Works	1941-1962
10	Gravieside Paraffin Works	1863-1879
11	Brieich (West/Middle) Oil Works	1886-1902
12	Grange (Charlesfield) Shale Works	1864-1875
13	Blackburn Shale Oil Works	1867-1868
14	Seafeld Crude Oil Works	1874-1931
15	Boghall (Starlaw) Oil Works	1868-1882
16	Deans Crude Oil Works	1884-1956
17	Drumcross Paraffin Oil Works	1866-1868
18	Oakbank Paraffin Oil works	1863-1938
19	Pumpherston Oil works	1884-1962
20	Buckside/Pumpherston Shale Works	1863-1869
21	Roman Camps (Almondfield) Paraffin Oil Works	1865-1884
22	Drumshoreland Paraffin Works	1864-1868
23	Roman Camps Shale Oil Works	1864-1871
24	Roman Camps Oil Works	1891-1958
25	Stankyard Praffin Refinery	1865-1877
26	Uphall Stankyard Oil Works	1866-1931
27	Holmes Oil works	1884-1901
28	Broxburn (Stewartfield) Oil Works	1865-1871
29	Broxburn (Stewartfield) Oil Works	1865-1871
30	Broxburn Paraffin works	1863-1876
31	Hallfarm/Broxburn Oil Works	1870-1877
32	Broxburn (Greendykes) Paraffin works	1862-1878
33	Broxburn (Greendykes) Paraffin Refinery	1864-1878
34	Broxburn Paraffin works	1866-1873
35	Broxburn+ Albyn Oil Works	1864-1878
36	Hopetoun Oil Works	1872-1951
37	Niddry Castle Oil Works	1903-1963

Table 3.5 - The main oil shale works in the Almond River Catchment. Thirty seven of the most significant oil shale processing sites are outlined with the operational period of each given (numbers related to positions shown of Figure 3.9)

3.4 Oil shale processing waste

Oil shale waste is variable in colour ranging from black/blue through brown and yellow to orangey red and pink, however, orangey red is by far the most prevalent colour. As a bulk waste it varies from a fine sand of broken spent oil shale fragments to coarse gravel. The larger red orange fragments are fissile and can be broken relatively easily along the laminations of the shale, which have been exaggerated compared to the raw oil shale, by the application of the heat in the retort. The waste differs significantly from a typical coal waste, it has a much lower water holding capacity (Harvie 2005), and the shale is free draining and relatively porous (Winter 2001). Also, the size difference between oil shale waste and coal sites is striking with sites reaching up to 95m high (Table 3.6) and often containing many millions of tonnes of waste.

Within the Almond catchment no significant oil shale waste sites containing only *normal* overburden material, derived directly from the mining process, have been identified. There are, however, variable but significant quantities of black grey shale at most of the oil shale waste sites. It is thought most *normal* mine over burden waste from the oil shale mining process was incorporated within the spent/burnt red orange oil shale bings. It is likely much of the discarded black grey shale is infact ‘blaes’ or inferior oil shale which was mined during mine development but was also occasionally mistaken for true oil shale but was of little use for hydrocarbon extraction. Therefore, oil shale waste sites in West Lothian consist predominantly of processed red orange oil shale waste with a minor proportion of black unprocessed oil shale mine waste .Evidence of this can be seen at several oil shale waste sites in the Almond Catchment (Figure 3.8)

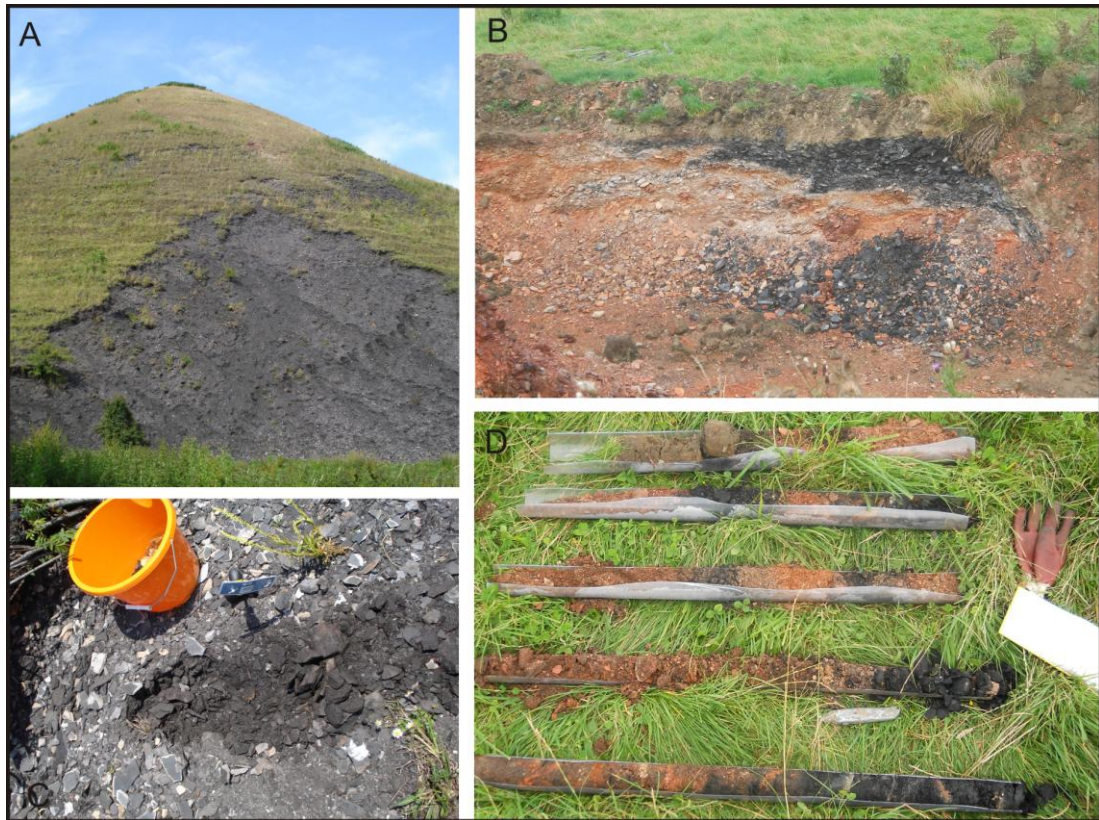


Figure 3.8 - Examples of black shale waste at oil shale waste sites in the Almond River Catchment. **A**-one of the spoil heaps at the Five Sisters oil shale bings showing a predominance of grey shale. **B**- black shale horizon at the Hermand oil shale bing. **C**-black grey shale on the surface of the Five Sisters oil shale bing. **D**- orange, brown and black horizons of oil shale waste in windowless sampling tubes recovered from the Hermand oil shale site (Chapter 5).

On the current West Lothian landscape there are 19 oil shale bings, 16 of which are within the Almond Catchment (Table 3.6, Figure 3.9). This is less than the 27 originally present at the end of the oil shale industry because several were removed and used as fill in construction projects including the M8 and M9 motorways. Orange red spent oil shale can be found all over the West Lothian landscape in back gardens and as small tips next to historic mineral railways as well as small fragments on the river bed and banks of the River Almond.

	Name	Closure Date	Height (m)
A	Addiewell North	1932	9
B	Addiewell South	1932	30
C	Greendykes	1925	95
D	Drumshoreland North	1925	61
E	Clapperton	1925	38
F	Drumshoreland South	1925	61
G	Oakbank	1932	46
H	Mid Breich	1915	12
I	Five Sister	1962	91
J	Fauchledean	1925	31
K	Niddry	1961	61
L	Albyn	1925	46
M	Green Bing	1920	61
N	Stankards	1920	61
O	Seafield	1932	53
P	Deans	1946	76
Q	Hermand	1894	8

Table 3.6 - Table of the main oil shale bings or waste sites in the Almond River Catchment. Eighteen waste sites are identified with the closure date of each and the height relative to the surrounding area (From Harvie 2005)- (Letters correspond to Bing locations shown on Figure 3.9).

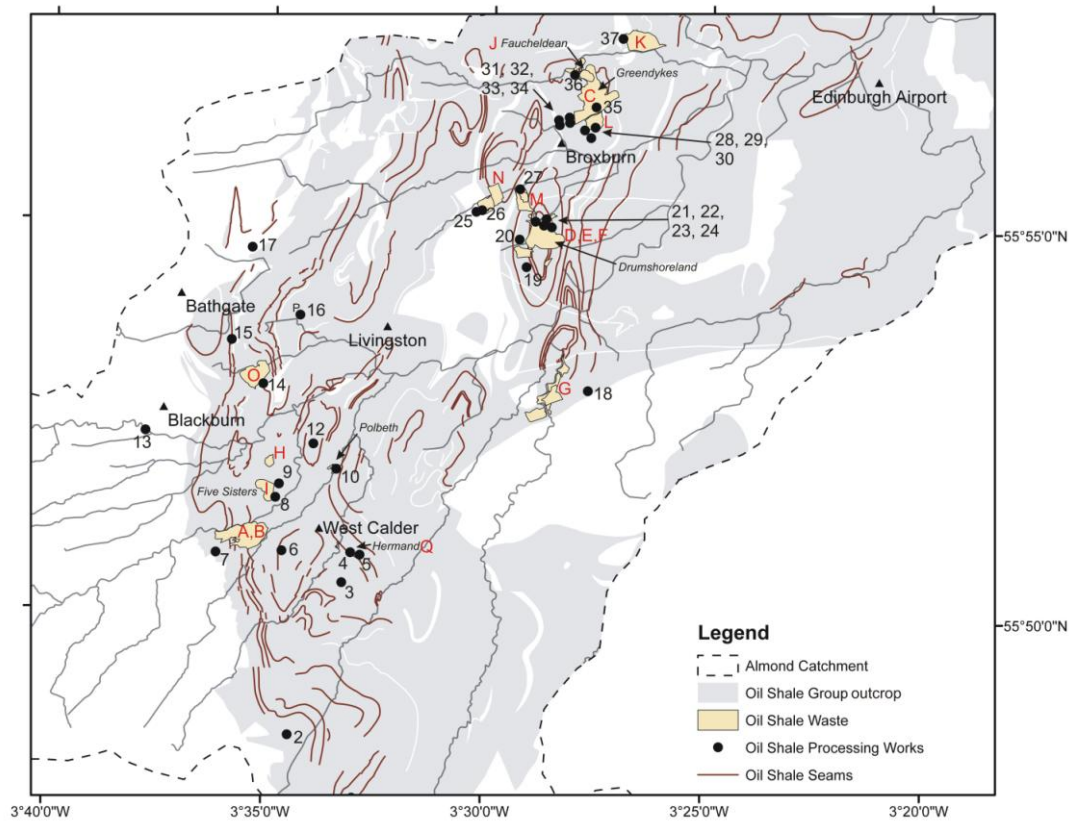


Figure 3.9 - Oil Shale Processing Facilities, Oil Shale Waste 'Bings' and Shale seams in the Almond River Catchment. The red letters correspond to the 'Bings'/waste sites in Table 3.6. The faulted and folded arrangement of the approximately 20 oil shale seams is shown by the red lines on the grey oil shale outcrop area. The processing sites from Table 3.5 are also shown.

3.4.1 Waste mineralogy and chemistry

The mineralogy of six of the oil shale waste sites (bings) in the Almond Catchment was investigated by the collection of composite samples with a trowel and bucket from the top 50cm at 30 evenly spaced locations across the waste site according to the method outlined by Smith et al. (2000). The composite samples were sieved, crushed, powdered and analysed in the University of Edinburgh by the method outlined in Chapter 5. The mineralogical analysis is presented in Table 3.7 and a typical XRD trace is shown in Figure 3.10. Two of the samples, Greendykes and Drumshoreland, were also selected for major and trace element analysis by ICP-MS which was conducted by BGS, UKAS accredited laboratories. The results of this analysis are presented in Table 3.8. Presented also, in Table 3.9 is a summary of soil nutrient data from 4 oil shale waste sites in West Lothian originally presented by Harvie (2004). This nutrient data is effectively leachate data obtained by mixing samples with weak acid and analysing the resulting fluid by flame atomic absorption spectroscopy.

	Faucheldean	Faucheldean Red	Faucheldean Black	Five Sisters	Polbeth	Greendykes	Drumshoreland	Hermand*
Quartz	18	15.59	15.5	28.4	29.6	9.5	19.2	30.3
Calcite	1.34	2.78	6.4	-	-	6.9	4	0.68
Dolomite	1.56	-	-	0.98	0.76	-	-	0.89
Hematite	8.7	12.13	-	1.79	12.3	9	6.31	8.29
Muscovite	23.3	44.91	35.4	40.9	19.3	13.9	45.16	18.55
Kaolinite	-	-	1.1	4.4	1.5	-	2.25	0.98
Albite	14.9	7.1	19.2	Tr	3.8	20.8	7.5	2.39
Anorthite	14.3	2	12.1	-	2.3	23.4	15.5	7.85
Microcline	6.6	13.7	10.4	2.5	2.6	9.4	-	3.6
Orthoclase	-	-	-	5.5	1.9	3.6	-	-
Mullite	-	-	-	6.3	21.9	-	-	28.1
Corderite	-	-	-	-	-	-	-	4.36
Other	3.3Mi	-	-	1.1Mi	4.2Sd	-	-	-

Table 3.7 - XRD analysis of selected oil shale waste bing material in wt%- Mi=mica, Sd=siderite. The main mineralogical abundances of each of the composite samples recovered from the upper cms of the waste sites are described. *these data are the median of 19 analysed samples collected at a variety of depths within the Hermand waste pile.

Table 3.7 indicates that the mineralogy of the waste is variable but that all the sampled wastes sites consist predominantly of quartz, hematite, muscovite and feldspar minerals of variable proportions. All the sampled wastes contain low quantities (1-4%) of carbonate minerals, either calcite or dolomite. Three of the sites

(Five Sisters, Polbeth and Hermand) contain mullite which is metamorphic mineral that is relatively rare in the natural environment but is a common refractory mineral. XRD analysis on the black shale sample 'Faucheldean' consists of aluminosilicates, quartz and carbonates.

	Greendykes	Drumshoreland
Al	124452	124800
Fe	70861	63098
Ca	35696	39267
K	21109	19971
Mg	13867	12628
Na	11355	6247
P	2235	1841
S	2025	2448
Mn	831	854
Zn	130	126
Ni	110	104
Pb	31.9	26.3
As	30.8	22.5
Cd	0.38	0.26

Table 3.8 - Major and trace element chemistry in mg/kg of two oil shale waste sites. Analysis undertaken by the British Geological Survey Laboratories Keyworth.

Table 3.8 indicates that the major element chemistry of the sampled oil shale waste sites is dominated by aluminium, Al, and iron, Fe. This is consistent with the mineralogical data which indicates that the waste is dominated by aluminium silicate feldspar minerals and iron bearing hematite. Calcium, magnesium, potassium and sodium are also of significant proportion and are likely to be bound in the clay, feldspar and carbonate mineral content of the shale. Of particular significance is the very low sulphur content of the waste at 2025-2448mg/kg or 0.2-0.24% compared to the sulphur content of the raw oil shale (median 1.25%, range 0.44-2.04%, Table 3.2). The low sulphur content is consistent with the non-detection of a sulphur bearing mineral in the XRD analysis for the same sites. The trace element chemistry of the oil shale indicates low levels of some potential eco-toxic elements namely Cd, As and Pb. Mercury (Hg) was not analysed.

	pH	Na	Mg	K	P	Ca	NH ₄ ⁺	NO ₃ ⁻
Min	5.72	1	16	5	5	50	0.05	0.03
Max	8.17	275	1289	371	180	20300	0.47	4.67

Table 3.9 - Selected plant nutrient chemistry in ppm (equivalent to mg/kg) of Oil Shale Waste originally presented by Harvie (2004)

Table 3.9 indicates that the oil shale waste substrate, as sampled by Harvie (2004, 2005), has a generally near neutral to alkaline pH and contains very low levels of nitrate and ammonium.

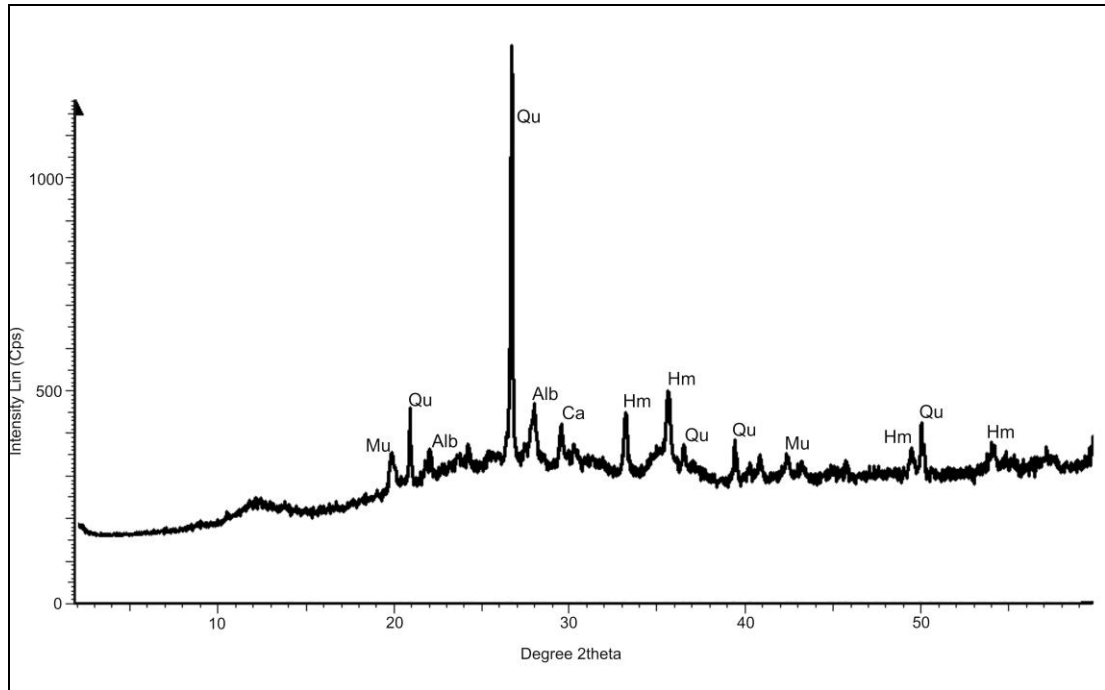


Figure 3.10 - XRD Trace from waste sample at Drumesshoreland Bing showing Qu-Quartz, Hm-Hematite, Mu-Muscovite, Alb- Albite and Ca-Calcite diagnostic peaks. The intensity reading on the left axis is arbitrary, the peaks correspond to the angle at which the x-rays were diffracted and are indicative of different mineral structures.



Figure 3.11 - Oil shale fragments recovered from the Faucheldean site showing red orange discolouration which is likely to be related of the oxidative weathering pyrite present in the shale. This is significant because it indicates that there is a proportion of unburned, potentially acid producing, oil shale on some of the waste sites in the Almond.

Evidence of oxidative weathering was observed on a small number of black oil shale fragments recovered from oil shale waste sites (Figure 3.11).

3.5 Contaminated land potential

The processing of oil shale is an activity from which there is a potential for significant ground contamination due to the accidental discharge of products or in the case of older sites, the occasional deliberate discharge of products associated with cleaning and maintenance activities. Unlike modern day hydrocarbon processing, which is heavily legislated, controlled and monitored, the oil shale industry operated in a time with effectively no environmental legislation (EASAC 2007). This means that the only incentive to prevent accidental discharge of products to the environment was to maintain profits. Also, in historic petroleum industries if inferior products

were produced, the easiest way to dispose of these was often to discharge them to the water environment.

3.5.1 Contaminant types

The Department of Environment (DoE) industry profile for '*Oil Refineries and bulk storage of crude oil and petroleum products*' identifies the Oil Shale Industry as a potential source of ground contamination. The principal contaminants of concern associated with extraction, refinery and storage of shale oil are organic hydrocarbon contaminants due to leaking of oil product from storage and distribution. A number of heavy metals are also identified as potential contaminants (DOE 1995).

Organic hydrocarbon contamination can manifest as a wide variety of potentially toxic chemicals depending on the composition of the hydrocarbon product. From the known list of products produced by the oil shale industry a number of potential contaminants have been identified;

- Petroleum Range Organics C4-C10
- Diesel Range Organics C12-C24
- Total Petroleum Hydrocarbons
- Benzene and related chemicals including ethyl benzene and benzo(a)pyrene
- Polycyclic Aromatic Hydrocarbons (PAH's)
- Volatile organic chemicals (VOC's)

These chemicals may manifest as soil vapours, free phase contamination in soils, on groundwater or as dissolved phase contamination in groundwater.

3.5.2 Evidence of contamination

Brock (1892) mentions several oil shale works where contaminated waters and 'tarry matters' were discharged from sites either directly or indirectly into the Almond River. While the majority of such contamination would have been dispersed through the river system long ago, this suggests that there may also be significant potential for ground contamination associated with processing sites. Furthermore, Brock's (1892) report makes mention of waters being passed through 'bing' materials (oil shale waste) as a form of filtration before discharged. No mention is given to the fate

of the collected sediment and sludge; potentially this may have been either buried or placed onto one of the oil shale waste sites. There is also clear evidence of leaks from storage facilities, *‘One of the works in Fife, the ‘Methyl Paraffin Oil works’, was under contract to supply products to a Newcastle merchant. The brick and cement tanks in which the oil was stored, prior to final purification were so poor that leakage from the tanks actually resulted in the company to fail’* (Redwood 1897). While this works was not in the Almond catchment, it was associated with the Oil Shale Industry and, therefore, indicates leaks are likely to have been common place. Oil shale retorting involved an array of pipe work to channel products from the retort to cooling, distillation and storage facilities, therefore, increasing the potential for accidental discharge to the environment.

The principal refinery in the Almond Catchment, to which the much of oil produced at retort sites may have been sent, was the Pumpherston Refinery (Figure 3.12). This site was in use from approximately 1870-1960, when it was replaced by a detergent manufacturing facility. The site has since been remediated but extensive contamination existed at the site which included polycyclic aromatic hydrocarbon contamination (PAH) in a number of hotspots in addition to surfactant contamination of the groundwater. (Bardos 2000)



Figure 3.12- Pumphreston Refinery prior to demolition and remediation. Several storage tanks likely to be for the produced oil products can be seen in the foreground. The railway lines brought in supplies to the factories and took away the products for distribution across Scotland and the rest of the UK. An oil shale waste site, probably formed from waste shale from the factory, is shown in the background (Reproduced with permission of the Almond Heritage Trust).

3.6 Discussion: the environmental legacy

The principal environmental issue associated with historic mining industries is the discharge of mine waters from flooded mines and mine wastes. However, at present mine waters from oil shale mines are poorly characterised and no notable investigations into mine water chemistry have been undertaken. Chapter 4 indicates that the oil shale mining areas contribute Fe and SO_4^{2-} to the river system; this could potentially be directly from flooded oil shale mines and mine waste discharges or diffusely from interactions between surface water and contaminated groundwater. In coal mines, seam sulphur, related to pyrite content, can be used as an indication of the potential for acidic, Fe rich, mine water discharge. The similarities between coal and oil shale geology suggest the same association can be used for oil shale mines.

The seam sulphur contents, consistently being between 1-2%, and pyrite content of up to 3wt%, suggests that abandoned flooded oil shale mines have the potential to discharge acidic waters. Specifically these data indicate that mines associated with the Camps seam, 2.04% -S, the Raeburn seam, 3% pyrite, and also the Dunnet seams, being closely associated with a marine band, are likely to discharge waters with the highest concentrations of Fe. Fortunately, based on the data in Table 3.3, the Camps seam is entirely un-mined and the Raeburn experienced only limited mining. The Dunnet seams, however, are amongst the most heavily mined in the region indicating the potential for the significant acidic generation and Fe discharge. The remainder of the worked seams, containing over 1wt% S and trace to 1wt% pyrite, also present a significant potential source of contaminated mine water discharge.

Mine water chemistry is influenced by the geology and mineralogy of the whole mine complex. In general the descriptions of Browne et al (1999) suggest that West Lothian Oil Shale formation is more sandstone dominant than the coal bearing Limestone Coal Formation and Scottish Coal Measures, which are known to contain mines which discharge significantly elevated concentrations of Fe and SO₄ (Younger 2001, Chapter 6). This could indicate that oil shale mines are likely to discharge lower Fe concentrations, since the highest pyrite concentrations are generally found in argillaceous rocks formed in reducing conditions. Ultimately these relationships are only indicative of the nature of water which might be discharged from flooded oil shale mines. The true nature can only be determined by sampling of oil shale discharges, chemical analysis and classification.

Comparison of raw and processed oil shale, for which mineralogical data presented in Table 3.1 and Table 3.7 respectively, indicates that the oil extraction method not only altered the organic proportion of the oil shale but also fundamentally altered its mineral content. Feldspar, mullite and corderite analysed within the waste mineralogy can only have originated from the dehydration and transformation of clay minerals due to the application of heat. The presence of mullite and corderite indicates that heating reached temperatures of up to 1000°C (Deer et al 1966, Grigore et al 2008). These temperatures are unlikely to have been optimal within the retort as

Bailey (1927) indicates that maximum ‘normal’ operating temperature reached in the retort were $\sim 700^{\circ}\text{C}$. Above this temperature unwanted ‘cracking’ of the hydrocarbon product would occur. Therefore mullite and cordierite formation is thought to represent overheating and fusing of the oil shale within the retort, probably associated with the early industry processing practices when temperature control was limited. Also continued burning of the shale on the bing was common place in the early industry. Mullite and cordierite are common refractory minerals with needle like structure which help to strengthen pottery (Deer et al 1966), therefore, they are likely to be responsible for the ‘fusing’ of the shale under excess heat.

Hematite in the waste, which results in the distinct red colour, must have formed from the destruction of iron bearing minerals, such as pyrite and siderite, in the unprocessed shale. Iron impurities within the abundant clay mineralogy may also have contributed to the hematite formation. Also, the low sulphur content of the waste compared to the 1-2% sulphur in the raw oil shale suggest that during the destruction of pyrite the sulphur content together with nitrogen is bound with steam and oxygen injected into the retort to form ammonium sulphate. This also accounts for the generally low nitrate and ammonium content of the waste recorded by Harvie (2004). The impact of processing on the oil shale mineralogy, chemistry and by-products is summarised in Figure 3.13.

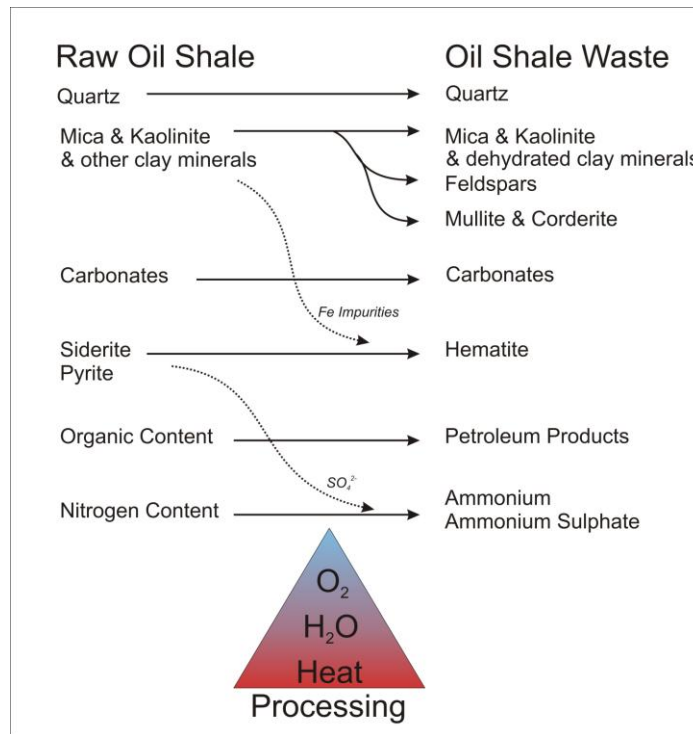


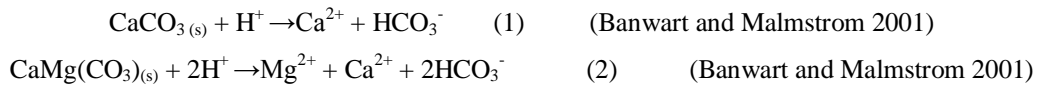
Figure 3.13- Illustrative diagram of the influence of processing within the retort on oil shale mineralogy. The diagram shows the main mineralogical phases identified in the raw oil shale to the left and the transition to the processed oil shale waste mineralogy to the right due to the application of heat, water and oxygen in the retort.

The mineralogical evolution of oil shale from a raw oil shale rock to the red burnt oil shale, whilst being significant from an industrial archaeology perspective also fundamentally alters the potential environmental impact associated with burnt oil shale waste in the Almond Catchment. As stated previously, pyrite content is the principal cause of concern associated with mine water discharge. The destruction of pyrite via the processing of the oil shale removes the principal potential mechanism of acid generation and heavy metal mobilisation. This is supported by the general alkaline nature of oil shale substrate reported by Harvie (2005). Several authors (Winter & Butler 1999, Winter 2001, Layden 2009) have previously suggested that while pyrite oxidation may not be significant sulphate release due to the presence of a significant sulphate mineral content in the waste may be of environmental concern. This suggestion by Layden (2009) is based on the mineralogy phase assemblage of oil shale waste from retorting, combustion and uncontrolled burning of Estonian oil shale (Puura 1999, Saether 2004) which differ in pre-processing mineralogy from the

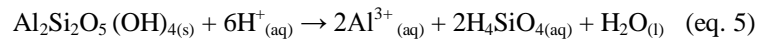
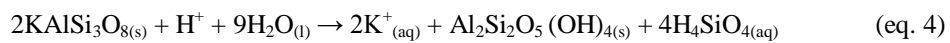
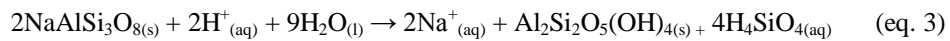
Scottish Oil Shales, while the suggestions by Winter (2001) and Winter and Butler (1999) are associated with limited evidence from adverse chemical impact of the shale on metal structures when the shale has been removed from the waste pile and placed elsewhere. There is no evidence from either XRD analysis or chemical analysis, presented in this study of significant sulphate mineral content in the processed oil shale waste.

While the orange red processed oil shale has had all of its pyrite removed via the heating process it is possible that the black shales found on the oil shale waste piles (Figure 3.8) may contain pyrite content. This is supported by the orange oxidative weathering identified on some of the black oil shale fragments (Figure 3.11).

The mineralogy data suggests that waters (H₂O) moving through the waste pile are likely to be impacted by increases in concentrations of calcium (Ca), magnesium (Mg) and bicarbonate (HCO₃⁻) as a result of weathering of calcite (CaCO₃, eq.1) and/or dolomite (CaMg(CO₃), eq. 2);

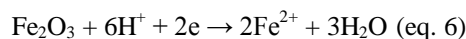


Sodium (Na), potassium (K) and aluminium (Al) concentrations may also be increased due to the weathering of feldspar (NaAlSi₃O₈, KAlSi₃O₈, eq. 3&4) and clay minerals (Al₂Si₂O₅(OH)₄, eq. 5).



(eq. 3,4,5, Lottermoser 2010)

The processed waste also contains high iron (Fe) content, in the form of hematite (Fe₂O₃), however, the potential for rapid release is limited as mobilisation would require a significant excess of proton acidity (eq. 6, Faust and Aly 1981); .



In summary the historic processing of the oil shale has significantly reduced the potential environmental impact of oil shale waste compared to raw oil shale which contains up to 3% pyrite. There is, however, some evidence of raw oil shale, or blaes, on the oil shale waste piles in the Almond Catchment. Oxidation of pyrite in the black shale may result in the limited release of Fe, SO₄ and acidity. The potential environmental impact of this will depend on the quantity of un-burnt shale within each site. Furthermore, there is evidence from elsewhere in the UK that shale (unburnt) waste sites may discharge Na-Cl dominant waters due to the flushing of residual pore waters (Banks et al. 1997)

The evidence presented here suggests that the discharge of waters from oil shale mines might be of similar or slightly reduced environmental concern compared to coal mines. The processing and resulting alteration in mineralogy of oil shale results in a waste which is likely to be of significantly less environmental concern than acidic mine waste often associated with coal mining, however, a potential significant quantity of black shale has been identified on waste sites suggesting the potential for contaminant release. The prevalence of oil shale processing in the catchment might also be a serious environmental concern due to the potential for hydrocarbon contaminated land.

The historic processing of oil shale and associated potential for surface water and groundwater contamination in the catchment was completely unregulated. Public health reports indicate that hydrocarbon contamination was prevalent throughout the Almond River due to the discharge of contaminated water used in processing. Extensive hydrocarbon ground contamination was encountered at the Pumpherston refinery which processed oil shale and shale oil products from elsewhere in the catchment. It is considered likely that other historic processing sites (Figure 3.9) resulted in ground contamination and in the majority of cases no remedial action will have been undertaken. This, of course, depends on whether any redevelopment has taken place to date and whether this was prior to the implementation of Part 2A (contaminated land) of the 1990 Environment Act. If contamination is present then it

is likely that hazardous substances, as defined by the EU Groundwater Daughter Directive, such as benzene, benzo(a)pyrene and naphthalene are being released to groundwater in the catchment. Detailed site investigations would be required to properly define and quantify the potential environmental impact.

3.7 Conclusions

A number of conclusions about oil shale geology and the shale oil industry can be drawn from the analysis of historic information sources supplemented by the analysis presented in this chapter;

- West Lothian Oil Shale was formed in a Carboniferous aged lagoon associated with a larger graben basin in which the majority of the sediments of the Midland Valley were deposited. This lagoon was stratified and anoxic allowing the preservation of organic material washed in from surrounding coal and peat bog areas.
- Oil shale was discovered to yield a hydrocarbon product similar to free running crude oil on the application of heat within a retort originally designed by James ‘Paraffin’ Young in 1850. The world’s first commercial oil industry grew in West Lothian and the Almond Catchment as a result of this discovery. Mining and processing of oil shale was undertaken for over 100 years until closure in 1962.
- The industry while bringing significant development to West Lothian resulted in environmental impacts which persist to the present day.
- The mineralogy and sulphur content of the worked oil shale seams, together with the associated geology of the West Lothian Oil Shale Formation suggest that there is potential for the discharge of contaminated mine waters from flooded oil shale mines in the Almond Catchment.
- Oil shale mineralogy is fundamentally altered by the heating process used to extract hydrocarbons from oil shale. The resulting processed waste contains hematite and feldspar minerals as the result of the transformation of minerals in the raw oil shale. Crucially the heating process destroys the pyrite content of oil shale therefore negating the principal contamination mechanism associated with acidic mine water production. However, most oil shale sites appear to contain a significant proportion of black ‘unburnt’ oil shale.
- Evidence suggests that there is potential for environmental impact from hydrocarbon contamination associated with historic processing of oil shale.

3.8 Acknowledgements

Historic photograph images are reproduced with the kind permission of **Almond Valley Heritage Trust** (*Museum of the Scottish Oil Shale Industry*). The trust have also been extremely helpful in providing time and resource to me personally as well as producing an excellent website (<http://www.scottishshale.co.uk>, last accessed 22/10/2012) from which several information sources and references have been used.

Chapter 4

Mine distribution and water quality

Foreword

This Chapter describes the surface water quality in the Almond River Catchment and examines the relationships between heavily mined areas, diffuse pollution signatures and flow dependence of mine related contaminants. The chapter takes from a paper which is in now in press with the **Journal of Applied Geochemistry** (a paper copy is provided at the end of the thesis and an electronic copy of the published manuscript is presented in Appendix F). Principally, the recommended revisions for the manuscript focused on reducing the length of the paper; however, the full length paper is presented here because it contains relevant historical overview of mining industries in the Almond River Catchment. Some minor edits have been made, based on the recommendations of the reviewers, associated with the interpretation of water quality impacts in the oil shale mining regions of the catchment.

The key highlights of the paper are:

- A GIS map of coal and oil shale mining in the Almond Basin was constructed
- Water quality data confirms the detrimental impact of historic mining activities
- Surface water flow affects mine contaminant chemistry, behaviour and transport
- Diffuse river bed Fe precipitates are transported downstream at high flow
- Oil shale mining is confirmed as a contributor to poor surface water quality

(Some of the preliminary results in this chapter were published in a conference proceedings paper for the International Mine Water Association Conference in Aachen 2011. A copy of the proceedings paper is included in Appendix F)

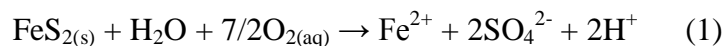
4.1 Abstract

The Almond River Catchment in Central Scotland has experienced significant historic coal and oil shale mining during the last 300 years. Detailed spatial analysis of the catchment has identified over 300 abandoned mine and mine waste sites, comprising a significant potential source of mine related contamination. River water quality data, collected over a 15 year period from 1994 to 2008, indicates that both the coal and oil shale mining regions detrimentally impact shallow groundwater and surface water quality long after mine abandonment, due to the continued release of iron and sulphate associated with pyrite oxidation at abandoned mine sites. Once in the surface water environment iron and sulphate display significant concentration-flow dependence: iron increases at high flows due to the re-suspension of river bed iron precipitates ($\text{Fe}(\text{OH})_3$); sulphate concentrations decrease with increased flow as a result of dilution. Further examination of iron and sulphate loading at low flows indicates a close correlation of iron and sulphate with mined areas; cumulative low flow load calculations indicate that coal and oil shale mining regions contribute 0.21 and 0.31 g/s of iron, respectively, to the main Almond tributary. Decreases in iron loading on river sections demonstrate the deposition and diffuse storage of iron within the river channel. This river bed iron is re-suspended with increased flow resulting in significant transport of diffuse iron downstream with load values of up to 50 g/s iron. Interpretation of major ion chemistry data for 2005-6 indicates significant increases in Ca^{2+} , Mg^{2+} and HCO_3^- in coal mined areas probably as a result of the buffering of proton acidity in mine waters; in the oil shale areas increases in Na and Cl are observed. The study demonstrates the cumulative impact of point and diffuse contamination sourced from numerous small and several large coal and oil shale mine sites on surface water iron load and whole water quality.

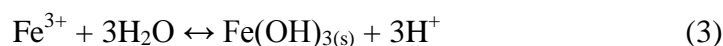
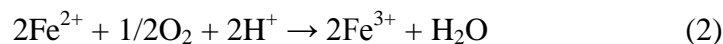
4.2 Introduction

Production of heavily mineralised discharge waters is a phenomenon observed world wide at active and abandoned mine sites (Wood et al. 1999, Blowes et al. 2003). Mine closure commonly results in increased concentrations of dissolved ions in discharge waters, compared to pre-closure concentrations (e.g. Banks et al. 1997, Younger 1998, 2000a), caused by groundwater rebound, subsequent flooding of the mine void and increased mineral dissolution. The discharge of these mine waters can have serious environmental consequences for the recipient rivers, surface water and groundwater bodies (Younger 1995, Banks et al. 1997). Waste rock brought to the surface in the process of mining can also produce similar mine waters on exposure to atmospheric oxygen and precipitation (Rees et al. 2002).

Coal mining is widespread throughout the UK and Europe. Risks to the environment from abandoned coal mining and the mechanisms of contaminant production are, therefore, well studied and characterised (e.g. Wood et al. 1999, Younger 2000a, 2000b, 2001). Contaminant production in the form of elevated levels of iron, Fe^{2+} , and sulphate, SO_4^{2-} , in mine waters has widely been attributed to the oxidation of pyrite, FeS_2 , either by the ingress of atmospheric oxygen and/or dissolved oxygen, in waters, into a subsurface mine or at surface in mine waste. This can be expressed as:



The reduced iron species, Fe^{2+} , is generally stable in mine waters, due to reducing, oxygen poor conditions in the mine environment. Following discharge to the oxygen rich surface water environment, Fe^{2+} , is rapidly oxidised and precipitated leading to the formation of iron precipitates, $\text{Fe}(\text{OH})_3$ as shown by equations 2 and 3:



Fe precipitates are found suspended in the surface water column and as smothering river beds precipitates, generally when total Fe exceeds 0.5mg/L (Younger 2000b). This reduces light penetration to primary benthic producers leading to ecological impoverishment and wider water quality impacts (Jarvis & Younger 1997; Mayes et al. 2008). Other metals (Al, Zn, Cd, Cu and Ni), which are can be more ecotoxic than

iron, may also occur in mine waters, particularly at low pH, however, iron is generally the most abundant contaminant in the majority of mine water types (Hedin et al. 1994, Younger 1995, Banks et al, 1997) and is the main source of surface water ecological damage (Jarvis & Younger, 1997). Elevated concentrations of Mn and sulphate are also common and may be of concern in the surface water environment. Proton acidity, H^+ , is a product of pyrite oxidation (eq.1), however, levels of acidity are usually mitigated in discharge waters by carbonate mineral reactions in the mine; a process termed ‘carbonate buffering’ (Banks et al. 1997). In Scotland, where most coals are associated with carbonate rich coal measure rocks, such as limestone, mine waters are generally maintained at a circum-neutral pH (Younger 2001). Mine waste sites, however, usually produce more acidic discharge waters due to reduced availability of carbonate minerals in the mine waste pile (Rees et al. 2002).

The environmental impacts of oil shale mining, particularly in the UK, are poorly characterised compared to coal and other, more common, forms of mining. Oil shale and coal bearing rocks have similar pyrite content, normally around 1-2% (Louw and Addison, 1985), and both are associated with marine limestones (Francis, 1983). Pyrite oxidation and carbonate buffering reactions are, therefore likely to be the principal control on the chemistry of oil shale mine discharge waters. Oil shale mines in Estonia (Erg, 2005) have been documented as producing contaminated waters similar to those associated with abandoned coal mines.

Oil shale was mined in Scotland to extract the organic fraction of the shale as a form of crude oil. This was achieved by exposing the mined rock to temperatures above 500°C in large scale industrial chemical processing plants (Carruthers et al. 1927). Exposing the shale to these temperatures is likely to have oxidised any pyrite or other sulphide minerals. Therefore, the risk of pyrite oxidation as a trigger for contaminant production in the resulting burnt processed waste is considered to be low (Sherwood 1994; Winter 2001). Oil shale waste has been noted to contain significant amounts of iron- Fe_2O_3 -12% and sulphur- SO_3 -3.2% (Burns 1978). Weathering of the processed oil shale waste, however, is unlikely to result in the release of iron and sulphate in discharge waters. Over burden oil shale mine waste derived from the mining, which

was not heated, may have the potential to produce contaminated mine waters, through pyrite oxidation.

In recent years significant advances have been made in the assessment of mine water hazard and impact as well as in remediation technology design to reduce the impact of point source mine water contamination on surface water and groundwater (Younger 1995, 2000a, 2000b; Jarvis et al. 2006). Point sources are individual mine water discharge streams at mine site, usually associated with a historic mine structure such as a shaft or adit. Diffuse pollution sources, as stated by Mayes et al (2008), include (1) diffuse seepages in the immediate vicinity of point discharges (e.g. Howes and Sabine, 1998), (2) direct input of polluted groundwater to surface waters, via the hyporheic zone (e.g. Gandy et al. 2007), (3) runoff from spoil heaps rich in sulphide minerals (e.g. Jarvis et al. 2006) and (4) re-suspension of metal-rich riverbed and bank sediments (e.g. Cravotta and Bilger 2001). Dealing with the cumulative impacts of numerous point and diffuse mine contamination within heavily mined river catchments has, on the whole, received less attention than individual point mine water sources. Recent European (Water Framework Directive; 2000/60/EC) and national legislation (Water Environment and Water Services Act (Scotland) 2003) encourages consideration of water quality pressures on the river catchment scale and the scientific community is increasingly advocating this scale of approach to deal with mine related contamination (eg. Kimball et al. 1999, 2000; España et al. 2005, Mayes et al. 2008). Understanding the combined impacts of mine sites, which in the case of coal and oil shale rarely exist in isolation due to the nature of their geological occurrence, is therefore considered key to improving water quality in the coal measure dominated river catchments of the central belt of Scotland, as well as those in northern England, southern Wales and across Europe.

The Scottish environmental regulator, SEPA, monitors water quality across Scotland to identify pressures on the water environment. The Almond River Catchment, on which this paper focuses, has long been highlighted as an area where water quality continues to be detrimentally impacted by elevated Fe concentrations, indicative of historic mining activity (Pollard 2001; SEPA Forth Area Management Plan).

Groundwater monitoring is also undertaken across Scotland, however, no reliable long term monitoring boreholes are available in the Almond River Catchment. Surface water quality is therefore the only reliable indicator of groundwater quality in the Almond catchment aquifer bodies.

The aim of this chapter is to assess the impact of historic coal and oil shale mining on surface water quality and characterise the flow dependency of mine water contaminants in the surface water environment. This is done by the construction of a GIS data base of historic mines in the catchment and correlating this to the source and transport of mine-related contamination in surface water under variable flow conditions. Over 15 years of surface water quality data from 19 points in the catchment, with corresponding river flow data, are analysed focusing specifically on Fe and SO₄, as the products of pyrite oxidation at mine sites, supported by pH, dissolved O₂ and major ion data.

4.3 Study area

The Almond River Catchment is located in the central belt of Scotland, between Glasgow and Edinburgh (Figure 4.1). The catchment comprises of approximately 370 km² of mixed urban and semi-agricultural land, of which up to 50%, by land area, has been affected by variable amounts of historic mining activity. Both coal and oil shale were mined in the catchment; coal from pre 17th century to the mid 1980's and oil shale from 1860's to the 1960's. The mining industries and the legacy of abandoned mine sites has resulted in significant impacts on surface water and groundwater quality in the catchment. Surface water quality is amongst the worst in Scotland (Pollard et al., 2001) and the overall quality status of surface water and groundwater is classified by SEPA as poor (SEPA, 2009-2015).

Historic mining was intensive and widespread with over 300 sites relating to the extraction or disposal of mined or quarried mineral resources, the majority of which relate to coal and oil shale mining, although less amounts of ironstone, limestone, slate, sandstone, metals and clay were also mined. Mine waters and the resulting surface water and groundwater contamination are not associated with every mine

site, however, the number and density of abandoned mine sites in the catchment gives an indication of the scale of potential environmental impact (Figure 4.2).

4.4 Geology

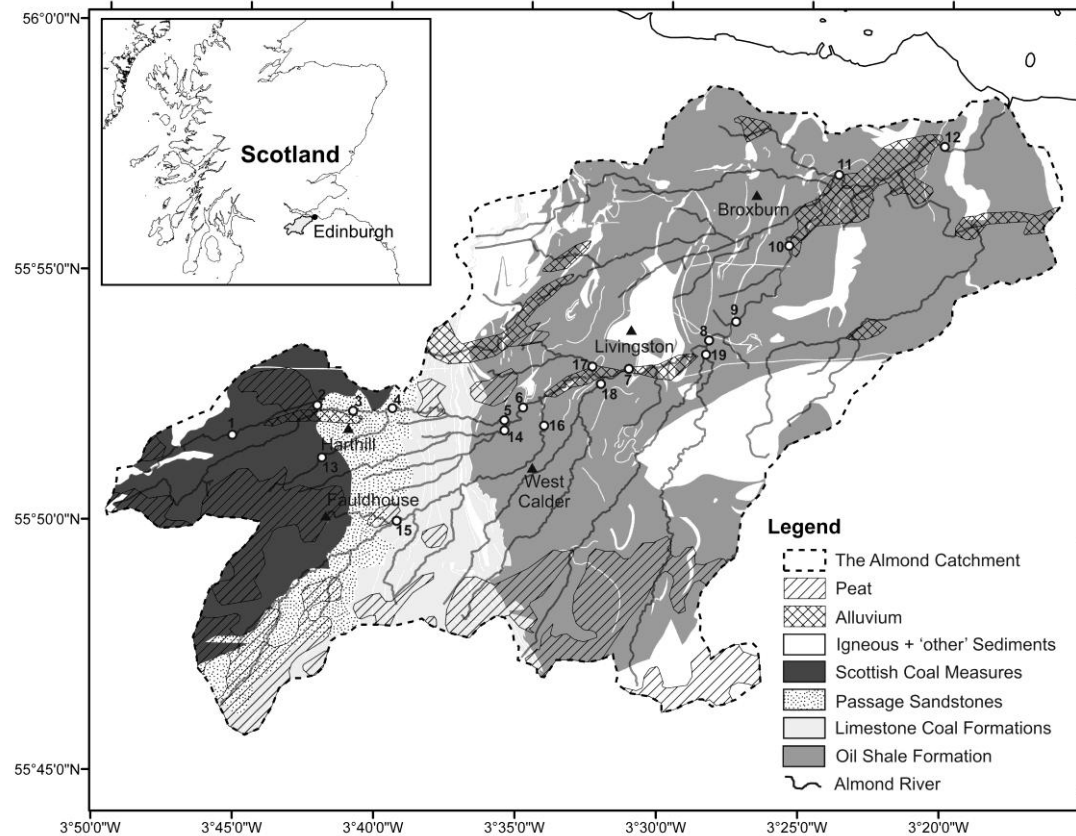


Figure 4.1 - The sedimentary geology of the Almond River Catchment is shown together with the Almond River and its tributaries as well as selected superficial geologies- peat and alluvium. The catchment geology is dominated, in the central and east, by coal measure type rocks consisting of interbedded sandstones, mudstones, shales, coal, occasional limestones and seat earths. The rocks of the oil shale formation to the west are similar but also contain up to 20 discrete seams of oil shale. The surface water monitoring network used in this chapter is also shown by the 19 numbered points on the Almond tributaries. Derived from BGS digital geological mapping at 50,000 scale, British Geological Survey © NERC. Contains Ordnance Survey data © Crown Copyright and database rights 2012

The Almond River catchment geology is dominated by a series of thick marine and deltaic Carboniferous aged sedimentary deposits (Table 4.1), part of the larger sedimentary sequence which composes the rocks of the Midland Valley, Scotland. The sediments appear in depositional cycles representing changes in the depositional regime of the Carboniferous sedimentary basin in which they were deposited. Principally, these cycles represent regressions from shallow marine to terrestrial

environments coupled with periodic rises in sea level and local and regional subsidence defined by the Southern Uplands and Highland Boundary fault. The present day complex outcrop structure (Figure 4.1) was caused by significant folding and faulting associated with a complex structural and volcanic history in the region (Francis 1983, Cameron and Stephenson 1985). The geology of the catchment is significant because it provides the framework for the mine site distribution and therefore contaminant source distribution.

Period	Group	Formation	Description	Map Reference
Upper Carboniferous	Coal Measures (Scotland)	Middle Coal Measures	Cyclic sequences of sandstones, siltstones, mudstones, ironstones, coals and seatrocks	Coal Measures
		Lower Coal Measures	Cyclic sequences of sandstones, siltstones, mudstones, ironstones, coals and seatrocks	
	Clackmannan Group	Passage Formation	Mainly sandstones with fireclays and thin siltstones, mudstones, ironstones and thin coals	Passage Sandstones
		Upper Limestone Formation	Cyclic sequences of sandstones, siltstones, mudstones, marines limestones and a few coals	Limestone Coal Formations
		Limestone Coal Formation	Cyclic sequences of sandstones, siltstones, mudstones, ironstones, coals and seatrocks	
		Lower Limestone Formation	Cyclic sequences of sandstones, siltstones, mudstones, marines limestones and a few coals	
Lower Carboniferous	Strathclyde Group	West Lothian Oil Shale Formation	Mainly sandstones with siltstones, mudstones and oil-shales, thin coal seams and limestones	Oil Shale Formation
		Gullane Formation	Sandstone, grey and green, siltstone and mudstone	'Other Sediments'
	Inverclyde Group	Ballagan Formation	Sandstone, grey and red, siltstone, mudstone and dolomitic limestone	
		Kinneswood Formation	Sandstone, pink, red-brown and white with siltstone and mudstone	

Table 4.1 - Geology and economic geology of the main Carboniferous aged deposits of the Almond River Catchment (after Francis, 1983, Cameron and Stephenson, 1985)

4.5 Data and methods

Extensive and detailed datasets of the geology and hydrogeology, water quality and land use history of the Almond River catchment were acquired from the British Geological Survey (BGS), Scottish Environment Protection Agency (SEPA) and West Lothian Council (WLC) respectively.

4.5.1 Spatial analysis

Mine datasets provided by WLC and the BGS were refined through field observations and analysis of historic data sources (Winter 2001; MacDonald et al 2003). Mine location data was refined sufficiently to be able to confidently identify the dominant mine types (i.e. subsurface, opencast or mine waste site) and mined mineral resources. Historic land use data were then compared, in ARC GIS, to the geological and hydrogeological data. Principle mining areas relating to different

mined resource were identified. Spatial comparison of field data and surface water quality data sets was then undertaken.

4.5.2 Water quality data

Comprehensive monthly to two-monthly sampling, dating back to 1994, is undertaken by SEPA at 19 monitoring points (Figure 4.1) on tributaries in the catchment, 1-12 on the main Almond tributary, 13-19 on second order tributaries. Sampled waters are analysed, by SEPA, for a number of analytical suites tailored to SEPA's requirements with respect to different water pressures including mining, urban drainage and sewage treatment. The data used in this study was extracted from this wider water quality data set in order to specifically consider mine water related water quality pressures (Data supplied by SEPA can be found in Appendix A). In general Fe_{tot} , pH and dissolved oxygen are available at all the monitoring points 1-19 in the catchment, sulphate was available at selected monitoring points (1-6, 10 and 12) on the main Almond tributary. Fe_{tot} is iron analysed in an unfiltered river water sample and therefore considers all the iron species in the sample, both dissolved and solid. Since 2007, a sample of Fe sampled through a $0.45\mu m$ filter has also been collected, $Fe_{<0.45\mu m}$, which is generally considered to only contain dissolved Fe species. These data are used to consider differences in Fe speciation in river waters.

River loads of iron and sulphate are calculated using daily flow readings from SEPA's 4 flow gauging stations in the catchment (Whitburn, Almond Wier, Almondell and Cragiehall). Flow readings (L/s) at the monitoring points (Q_c) are calculated by multiplying the flow reading at the nearest gauging station (Q_g) by a correction factor calculated from the relative catchment area (km^2) ratio of the monitoring point (C_c) and nearest gauging station (C_g).

$$Q_c = Q_g (C_c/C_g) \quad (1)$$

Where the catchment ratio (C_c/C_g) is close to 1 then the flow estimates and the associated load calculations are most accurate. This is generally the case for monitoring points 1-12 due to the proximity of monitoring points to gauging stations. Monitoring points 13-19 have lower catchment ratios and therefore give less accurate flow estimations and load calculations. As a result interpretations based on the load

calculations are generally only made using data from monitoring points 1-12, data from points 13-19 is used only to support these interpretations.

The concentration and load of contaminants are considered under low flow and high flow conditions in the river catchment. Low flow is defined here as flow values falling below the 30th percentile for the distribution of flow values recorded at each monitoring point during the monitored period (1994-2008 Fe, 1994-2006 SO₄²⁻); high flows are those flow values above the 90th percentile in the distribution.

Additional data on the concentration of major ions (calcium, magnesium, potassium, sodium, chloride, bi-carbonate, sulphate and nitrate) was also available for the years 2005-06 for monitoring points 1-12, this has been used to look at variations in the bulk river water chemistry in the Almond River.

4.6 Results & discussion

4.6.1 Mining and mine history

The scale and distribution of mining and the resulting mine waste across the Almond catchment is not uniform and several distinct areas of mining activity can be identified (Figure 4.2). Coal mining dominated in the south west of the catchment, targeting coals in the Scottish Coal Measures, Passage Formation and Limestone Coal Formations. Oil shale mining dominated in the central east of the catchment targeting the 6 workable oil shale horizons, the Pumpherston, Camps, Dunnet, Champfleurie, Broxburn and Fells seams in the Oil Shale group (Kerr 1994). The clear geographic divide between the coal and oil shale dominant mining regions is identified by the dashed line in Figure 4.2.

Early mining in the catchment targeted shallow accessible coal and oil shale seams and produced only small amounts of mine waste. Deeper mining, which produced increased mine waste and mine water volumes, came later as the result of advances in water technology (Duckham 1970) and increased demand in the coal market (Hassan 1976).

During the 19th century coal mining in Scotland saw considerable investment and growth however this wasn't reflected until after the 1840's in the mines of the Lothian coal fields (Hassan 1976) and the Almond River Catchment. After the 1840's, modernisation of the coal and transport industries and changes in the industrial and social landscape facilitated growth (Hassan 1976). Around this time in the 1850's innovations in hydrocarbon extraction technologies, by James Young, resulted in the mining and exploitation of oil shale deposits in the catchment and the growth of the oil shale industry. The coal and oil shale industries produced one of the UK's most heavily mined regions containing Scotland's most productive coal mine, Polkemmet (Oglethorpe 2006).

Opencast, shallow and deep mining was utilised over the lifetime of the coal industry. Most opencast mines were limited in their extent and were generally reinstated upon closure; no mine pit lakes occur in the catchment. Shallow coal mines were generally older, locally operated mines that although numerous were limited financially in their working depth, due to the expense of mining equipment and water pumps. Deeper mines such as, Polkemmet 1916-1984 (Shaft 2, 470m), Whitrigg 1900-1972 (Shaft 5, 323m), Riddochhill 1890-1968 (Shaft 1, 289m) came later in the early to mid-20th century and were managed on a much larger scale either by large private companies or by the National Coal Board (Oglethorpe 2006). The volumes of mine waste produced from coal mining although environmentally significant, due to the generally acidic nature, were smaller than the neighbouring oil shale industry.

The Oil Shale industry employed opencast, shallow and deep mining methods. The majority of early oil shale mines were opencast however 'inclined', or 'drift' type mines became common place as the industry developed. Pits or shafts, which were typically between 400-700 feet (120-210m), were used to intersect drift mines or to access deeper shale seams (Kerr 1994). Oil shale was mined and transported to the oil shale processing sites, of which there was over 100 at the peak of the industry, then the oil shale waste was deposited in large accumulations, known locally as 'Bings'. Almost the entire mined volume of the Oil Shale industry was deposited as

waste following the extraction of the oil shales' ~14% organic content (Yen and Chilingarian 1976). Estimates suggest there are 150 million tonnes of waste within West Lothian resulting from the Oil Shale industry (McAdam et al. 1992).

Oil shale mining went into decline in the early 20th century, due to competition from foreign oil, finally closing in the 1960's after the withdrawal of over forty years of government tax relief (Louw and Addison 1985). Coal mining continued until widespread UK closure began in the 1980's. Mine closure in the catchment has resulted in the production of numerous mine discharge waters from both subsurface mines and surface waste deposits.

The environmental impact of mining on the quality of river waters in the catchment today is both significant and widespread (SEPA 2009-2015), however the historic impact was noted back in the 1870's when fish stocks in the river were almost completely wiped out (Pollard et al. 2001). Coal solids being washed down-stream were also a serious historic problem. In 1892 (Brock 1892) when the medical officer of health for Mid Lothian was asked to survey the Almond River he described the river's extremely poor water quality;

'The water along its whole course has an ochry colour. Fish cannot live in it. Horses, cattle and sheep drink sparingly of it, if at all, and for industrial purposes it is almost useless on account of its destructive effects upon boilers.' W.J. Brock D.Sc (1892).

Improvements in working practices at mine sites and the decline in the processing of oil shale is likely to have improved water quality in the river waters in the latter half of the 20th century. However, closure of the coal mines in the 1980's only increased the environmental threat as the cessation of dewatering activities had the potential for the surface break out of iron rich mine waters (Younger 1994, Wood et al. 1999). The deep Polkemmet colliery is still pumped today, and the pumped water treated prior to discharge, to prevent the uncontrolled break out of mine waters at surface. Many of the smaller, older collieries were probably allowed to flood and produce mine waters which break out uncontrollably at surface following closure. Little to no

environmental management was put in place during the closure of oil shale mining activities as all were close prior to the 1960s. Significant advances have been made in recent years in improving water quality through mine water treatment schemes and remedial activities at old opencast and mine waste sites. However, historically the impact of mining activities was one of the principle factors in downgrading quality classifications on a large number of the Almond River catchment's tributaries (Campbell et al. 1996).

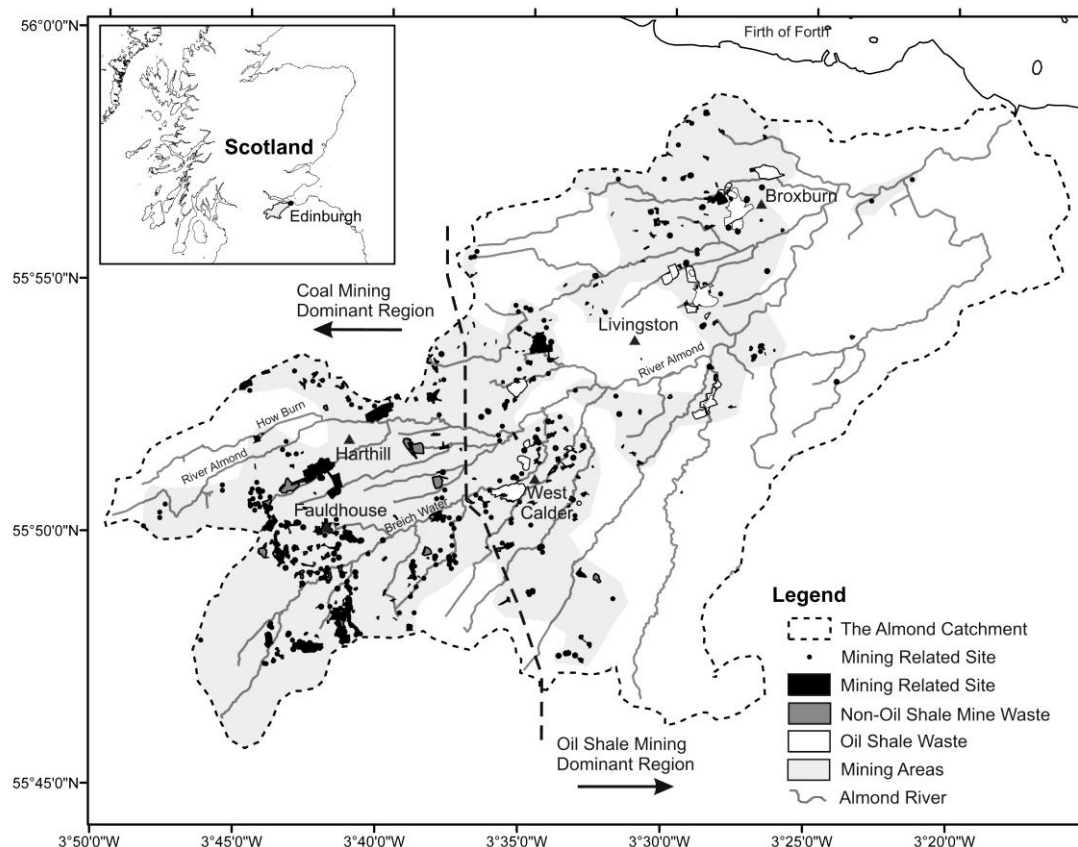


Figure 4.2 - Map of the mine site distribution in the Almond River Catchment. The divide between the oil shale and coal mining regions is shown. The mine sites are shown in black while the non-oil shale mine wastes (principally coal mine wastes but potentially also ironstone) are shown in grey. The oil shale wastes are shown in white. Contains Ordnance Survey data © Crown Copyright and database rights 2012

4.6.2 Water quality

Iron and sulphate data for the 19 surface water monitoring points in the catchment (12 on the main Almond tributary, 7 on smaller second and third order tributaries) are summarised in Table 4.2. Data indicates iron and sulphate in surface waters of the Almond basin are elevated compared to other rivers in Scotland (e.g. Soulsby et al., 2005, SEPA, 2009-2015). Neal (2011) presents average concentration data (Fe 0.13-0.54 mg/L, SO_4^{2-} 6-116mg/L) for river water in areas with similar geology but which are largely un-mined. Comparison of average Fe and SO_4^{2-} concentrations in the Almond River waters (Fe 0.64-2.64mg/L, SO_4^{2-} 96.22-244.19) to data presented in Neal (2011) indicates the impact of historic coal and oil shale mine sites on surface water quality caused by the discharge of elevated concentrations of Fe_{tot} and

SO₄²⁻ in mine waters associated with pyrite oxidation at the numerous mine sites in the catchment. The elevated concentration of Fe>0.5mg/L also indicates that river water ecology throughout the catchment is likely to be adversely impacted by Fe precipitate formation.

Fe _{tot}	1	2	3	4	5	6	7	8	9	10	11	12
Median mgL ⁻¹	1.27	1.20	1.59	1.30	0.88	1.18	1.30	1.02	0.92	0.79	0.78	0.68
Mean mgL ⁻¹	2.37	1.60	1.67	1.49	1.07	1.21	1.26	1.13	1.07	0.95	0.93	0.81
Max mgL ⁻¹	19.70	17.00	6.36	8.12	4.71	5.13	4.97	4.41	4.18	5.95	6.18	4.17
Low flow gs ⁻¹	0.01	0.04	0.09	0.07	0.07	0.10	0.31	0.39	0.39	0.26	0.28	0.37
High flow gs ⁻¹	3.06	4.68	9.45	9.71	10.10	15.38	30.16	50.27	46.62	49.06	50.40	34.74
SO ₄ ²⁻												
Median mgL ⁻¹	91.90	127.50	131.50	178.55	176.00	177.00	n.d.	n.d.	n.d.	124.00	n.d.	114.00
Mean mgL ⁻¹	96.22	132.13	132.45	244.19	230.74	192.44	n.d.	n.d.	n.d.	120.60	n.d.	113.89
Max mgL ⁻¹	196.00	240.00	217.00	686.00	572.00	525.00	n.d.	n.d.	n.d.	202.00	n.d.	186.00
Low flow gs ⁻¹	2.38	9.25	20.59	49.42	53.89	62.88	n.d.	n.d.	n.d.	161.19	n.d.	230.28
Fe _{tot}	13	14	15	16	17	18	19					
Median mgL ⁻¹	0.68	0.68	0.96	2.48	0.40	1.22	0.80					
Mean mgL ⁻¹	1.09	1.55	2.64	2.08	0.64	1.34	1.05					
Max mgL ⁻¹	6.15	33.00	5.83	19.00	3.93	7.82	6.44					
Low flow gs ⁻¹	0.01	0.04	0.31	0.21	0.01	0.06	0.04					
High flow gs ⁻¹	0.67	4.00	5.27	15.74	1.17	6.90	4.17					

Table 4.2 - Summary of over 15 years of concentration and load data for Fe_{tot} and SO₄²⁻ derived from SEPA analysis data sets on Almond surface waters. The load values have been calculated by multiplying the concentration and flow values derived from a SEPA hydrological data set.

4.6.3 Flow dependency

Concentration of Fe_{tot} and SO_4^{2-} in Almond surface waters (monitoring points 1-19) when plotted against river flow at the time of sampling show significant flow dependence (Figure 4.3). Fe_{tot} concentrations increase with increased flow while SO_4^{2-} concentrations decrease with increased flow. River water pH was also found to be flow dependent with lower pH values recorded at increased flow. All the monitoring points in the catchment were found to display these flow relationships.

At monitoring point 12 the relationship of Fe_{tot} to flow is approximated to a power law with an $R^2 = 0.635$. Flow dependence of Fe in surface waters has been observed, although over shorter monitoring periods with smaller distribution of flow values, in similar heavily mined catchments where it has been related to the re-suspension of diffuse sources of mine and non mine related river bed Fe sediments (Mayes et al., 2008). The flow dependence of Fe and the widespread mining in the Almond is also considered to be indicative of diffuse stream bed Fe precipitate re-suspension. Precipitate formation when mine waters are discharged to the surface water environment produces solid iron suspended in the water column; some of this is transported downstream while a large majority is deposited in surface waters close to the mine site. Indeed river beds covered in orange Fe are a common feature of the heavily mined areas in the catchment. However, because of the high density and long history of mining in the catchment, these river bed precipitates are considered to be almost ubiquitous throughout the main catchment rivers resulting in the flow dependency of iron at all monitoring points.

Sulphate concentration shows an opposing flow dependent relationship- sulphate concentrations are reduced with increased flow. Sulphate does not readily precipitate on exposure to oxygen and therefore does not commonly produce river beds precipitates. The flow dependence of sulphate is likely to be caused by dilution; the mass of sulphate in the river channel remains near constant while the river channel water volume and flow increase. The river water pH shows the same relationship to flow as sulphate. This is considered to be related to the difference in river water source at high and low flow. Groundwaters are generally the dominant water source

of river waters at low flow however at high flow rainfall and soil water sources dominant which have lower pH values than groundwaters.

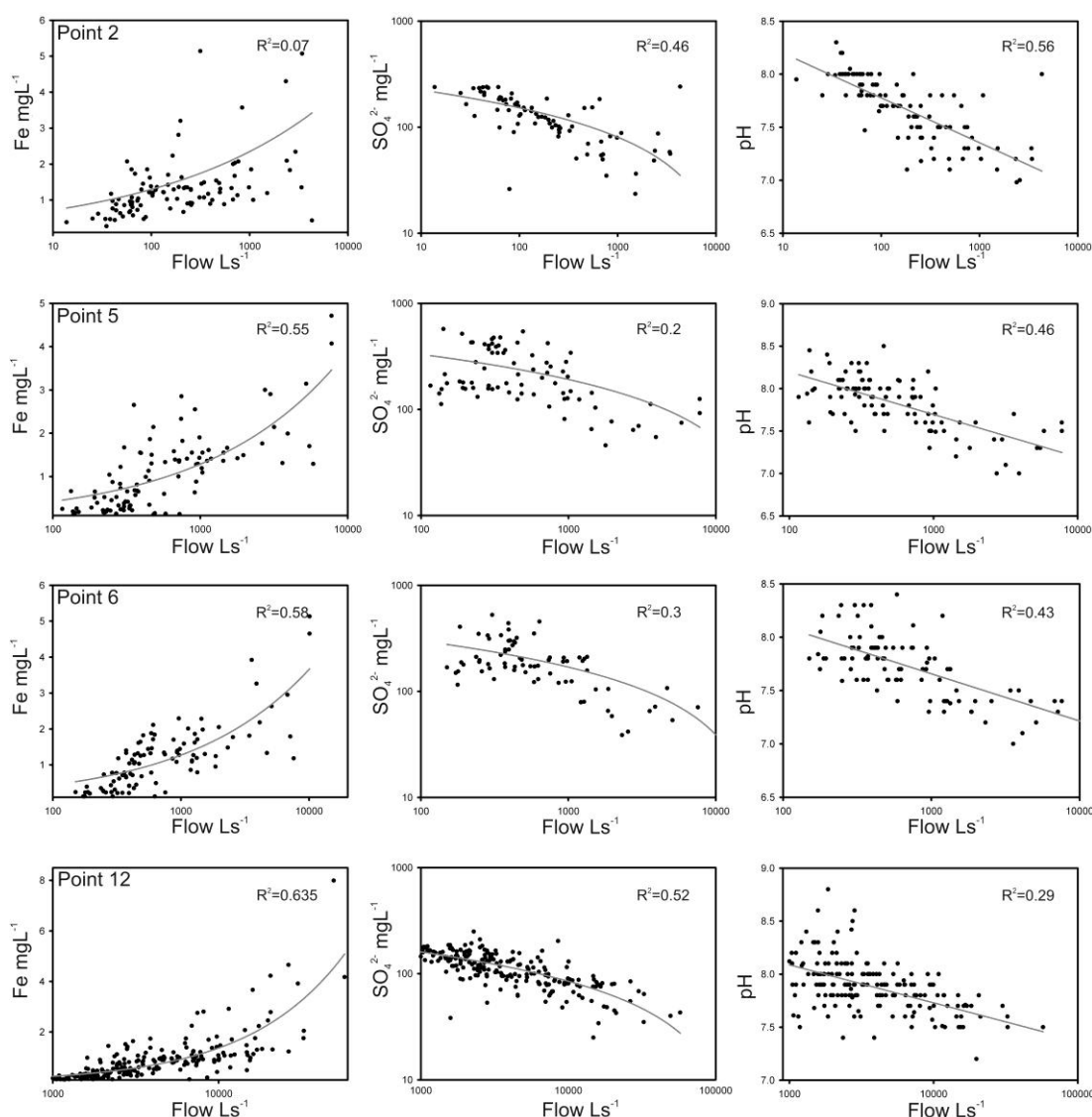


Figure 4.3 - Flow dependence of Fe_{tot} , SO_4^{2-} and pH in Almond surface waters derived from SEPA chemical analysis and hydrological data sets. The power law regressions applied to Fe vs flow plots show better R^2 correlations at monitoring points with larger catchment areas (e.g. point 12) due to the dominance of re-suspended river bed Fe from heavily mined areas. Monitoring points with smaller catchment (e.g. point 2) areas show a poor flow dependent relationship due to the greater significance of individual mine sites as point sources of Fe on surface water Fe concentrations

4.6.4 Fe speciation

Fe in mine waters discharged to oxygen rich river waters has a tendency to form $\text{Fe}(\text{OH})_3$ precipitates. Figure 4.4 shows the Almond surface waters plotted on an Eh-pH diagram with Fe species stability fields. No Eh data were available for the samples so dissolved oxygen measurements, ranging from 6-13mg/l, were used to estimate a mean Eh value of 0.5V to plot the results. This generally plots waters in the $\text{Fe}(\text{OH})_3$ region, although some of the higher Fe values are approaching the transition towards the Fe^{2+} region. This is significant because transition is generally graded between the Fe stability regions (Freeze and Cherry 1979).

Since 2007 SEPA have monitored river waters at a number of monitoring points for both Fe_{tot} and $\text{Fe} < 0.45\mu\text{m}$. Figure 4.5 shows the averaged low flow and high flow split between $\text{Fe} > 0.45\mu\text{m}$ and $\text{Fe} < 0.45\mu\text{m}$ and the corresponding pH. It should be noted that there is some indication that a $< 0.45\mu\text{m}$ filter, which is generally accepted to filter out all the solid chemical species in water sample, may allow small amounts of solid Fe complexes into the sample (Apello and Postma 2005). With this limitation in mind the diagram indicates that while Fe_{tot} increases at higher flow values related to the re-suspension of $\text{Fe}(\text{OH})_3$ described above, $\text{Fe} < 0.45\mu\text{m}$ also increase indicating a greater proportion of the dissolved iron species, Fe^{2+} . The reason for this $\text{Fe} < 0.45\mu\text{m}$ increase is related to the reduction in pH at high flow, shown by the pH values on the diagram and the relationship in Figure 4.3. The Eh-pH diagram of Almond waters (Figure 4.4) suggests the lower pH causes the partial dissolution of the re-suspended $\text{Fe}(\text{OH})_3$ as Fe^{2+} . The hydrological conditions in the river catchment, therefore, not only cause the re-suspension of diffuse iron, $\text{Fe}(\text{OH})_3$, but result in water chemistry changes which affect the behaviour of iron in surface water.

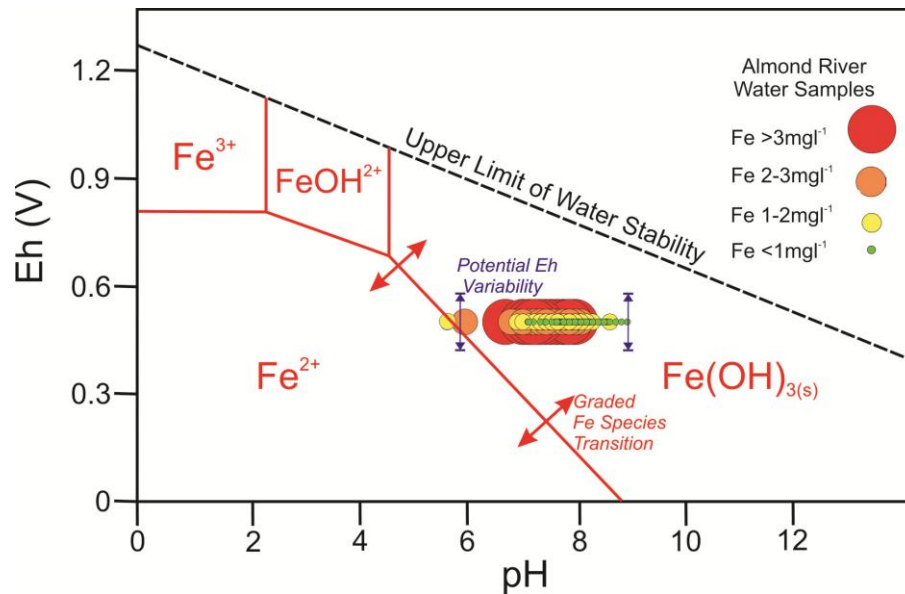


Figure 4.4 - Eh-pH diagram and Fe species stability in Almond surface waters. Individual samples are represented by the concentration graduated samples. The diagram indicates that higher concentrations of Fe, which occur during higher flow due to re-suspension of Fe precipitates $\text{Fe}(\text{OH})_3$, are likely to have a tendency to be dissolved as Fe^{2+} . This is supported by the relationships in Figures 4.3 and 4.5.

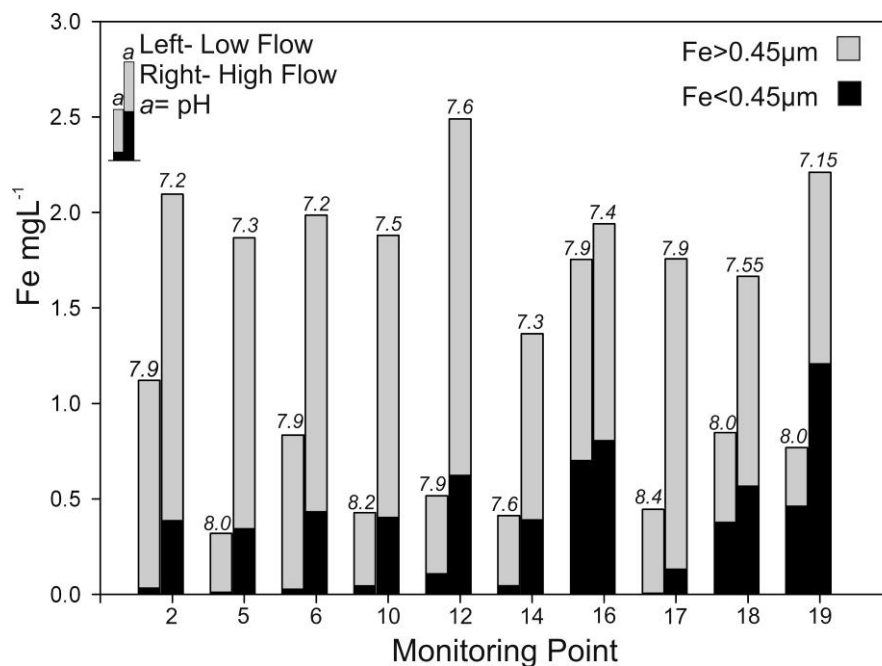


Figure 4.5 - Distribution of dissolved Fe, solid Fe and pH in Almond surface waters from 2007-2009. The bar charts show the difference between the average low flow and high flow split between solid and dissolved Fe analysed in river waters. In general the high flow shows higher concentration of Fe with a greater dominance of dissolved Fe compared to low flow values and a lower pH value.

The flow-concentration and pH relationship described above indicate that Fe and SO_4^{2-} concentrations in surface water will best represent direct impact of mining on water quality at low flow values. At higher flow values the input of iron from direct mine related inputs is likely masked by the re-suspension of diffuse sources of river bed Fe precipitates (Mayes et al. 2008). Iron concentrations at high flow maybe useful as an indication of the amount and location of the 'stored' river bed iron.

4.6.5 Iron and sulphate loading

Concentration data and averaged daily flow values have been used to calculate the surface water load of Fe and SO_4^{2-} in river waters across the Almond River Catchment (Table 4.2- Fe load- points 1-19, SO_4^{2-} load- points 1-7, 10 and 12). Load is defined here as a measure of the total mass of iron or sulphate passing each monitoring point. Figure 4.6 shows a box plot distribution of loading values for iron and sulphate at monitoring points 1-12 along in the Almond River during low flow events 1994-2008. The box plots for the load distribution at each monitoring point show the mean and 5th, 10th, 25th, 50th (median), 75th, 90th, 95th, percentiles. Geometric mean is used for the iron loading values due to the power law relationship of iron and flow outlined previously. The mean load value of the distribution at each point is joined by the dashed line to give a visual representation of the mean loading profile along the Almond River. An upward trend on the loading profile represents the input of fresh iron or sulphate, whilst a downward trend represents, in the case of iron, deposition of $\text{Fe}(\text{OH})_3$ from the water column to the river bed, or for sulphate, dilution.

The plots show between a 1 and 2 order magnitude increase in loading of both iron and sulphate from one end of the catchment (point 1) to the other (point 12). This is a clear indication of the discharge of iron and sulphate heavy mine waters, controlled by pyrite oxidation at the mine site, and the resulting impact on the quality of surface water.

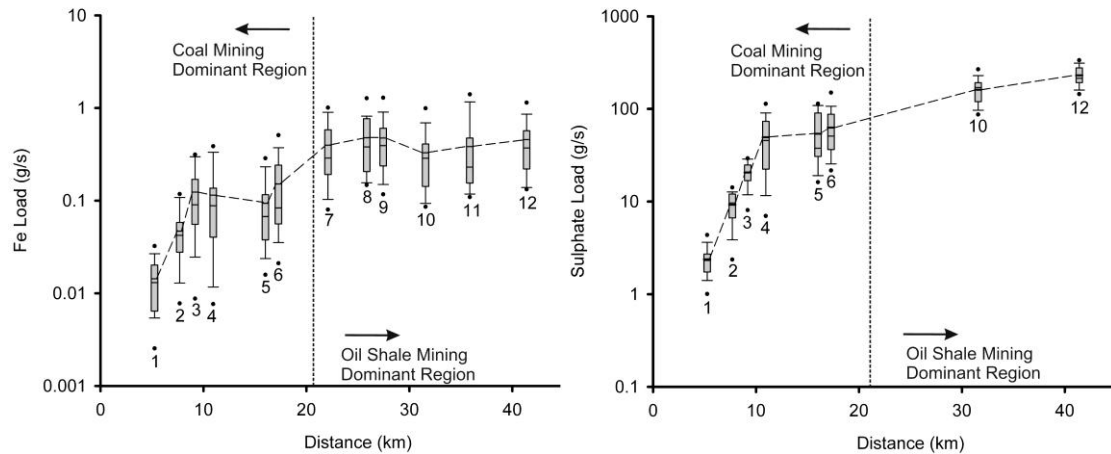


Figure 4.6- Box plots of the distribution of Fe_{tot} and SO_4^{2-} at Low Flow. The box plots show the max, min, median, average and 5th, 10th, 25th, 75th, 90th, 95th percentiles of the distributions of Fe and SO_4^{2-} load calculated from chemical analysis and hydrology data over a 15 year period from surface waters in the Almond. The geometric mean value of each distribution is joined showing a general increase in loading along the river but also reductions in iron loading where deposition of suspended Fe precipitates dominates.

The geographic divide and distribution of coal and oil shale mining (Figure 4.2) in the catchment allows the detailed interpretation of load increases calculated from water quality monitoring data. Figure 4.7 displays the low (A) and high flow (B) iron load distribution calculated at all 19 monitoring points across the Almond River Catchment. Sulphate loading is not included in Figure 4.7 as sulphate data was limited. Interpretation of iron and sulphate load profiles in Figure 4.6 and iron loading across the catchment in Figure 4.7 allows the identification of specific regions of concern or ‘hotspots’;

- Iron and sulphate load increases between monitoring points 2 and 3 (Fe- 0.04-0.09g/s, SO_4^{2-} - 127.5-131.5g/s) indicate the influence of mine waters from the ‘Harthill/Whitburn’ mining area on the Almond River prior to confluence with How Burn. The load differences between points 2 and 3 suggest approximate loads of Fe- 0.05g/s and SO_4^{2-} - 4g/s on the unmonitored section of the River Almond (Figure 4.7) sourced from the ‘Harthill/Whitburn’ region. Historic mining (particularly south of Harthill) was intensive and numerous coal mine sites and several mine waste sites discharge mine waters to the surface water environment (e.g. Heal and Salt 1999). Peat bogs on Polkemmet moor close to this area may also contribute as a non-mine

source of iron. High flow iron load between points 2 and 3 increases (from 4.68 to 9.45g/s) indicating the storage and re-suspension of diffuse river bed Fe precipitates upstream of point 3. Increases may also be attributed to increased run off from mine spoils sites as well as re-suspension of significant stores of associated Fe precipitates on small stream which were observed on field visits. However, other studies on similarly heavily mined catchments concluded increases in run off from mine spoils sites at high flow was of little influence on in-stream iron loads (Mayes et al. 2008).

- Iron and sulphate low flow loads, between points 5 and 6, increase significantly (Fe-0.03g/s, SO_4^{2-} -5.28g/s), likely due to the influence of mine waters in the ‘Bathgate’ and ‘Harthill/Whitburn’ coal mining regions. This is confirmed by the low flow iron load at point 14 of 0.04g/s demonstrating the influx of iron from these mining areas. The point source Polkemmet mine waters are discharged to surface waters in this region as well as a significant amount of contaminated waters from the large Whitrigg mine, where diffuse mine waste discharge waters contain significantly elevated levels of Fe and sulphate (Heal et al. 2006). High flow loads at point 14 of 4 g/s, which correlated with load increases between 5 and 6 of 5.28, also indicates the significant storage of diffuse river bed iron on tributaries in this area.

- Between points 6 and 7 low flow iron load increase of 0.2 g/s, is principally attributed to the influx of waters from the large second order tributary ‘Breich Water’ as well as the influence of smaller tributaries monitored at point 17 and 18 (Figure 4.2). ‘Harthill/Whitburn’, ‘Muldron Forrest’ and ‘Addiewell’ coal mining regions and ‘West Calder’ and ‘Livingston Village’ oil shale mining regions all potentially contribute a significant volume of mine waters discharged from mine sites as well as mine waters from the many coal and oil shale mine wastes in the region. Sulphate is not monitored at point 7 although a significant increase would be expected.

- ‘Breich Water’ runs through both coal and oil shale mining regions and is monitored at points 15 and 16. The iron load at point 15 is calculated at 0.307g/s which is considered to be elevated; however the load calculations here (and for all monitoring points 13-19) are likely to be less accurate than others in the catchment,

namely 1-12, due to their distance to the nearest flow gauging station. However, mean and median iron concentrations (2.480 and 2.640 mg/l), at point 15 indicate the significant input of iron. The 'Muldron Forest' region had numerous small, early mine sites as well as some significant larger sites such as Woodmuir Colliery and the Levenseat mine; minewaters from mines and mine wastes are common. Areas of peat bog in the region may also be significant in contributing to the iron loading.

- The reduction in low flow iron load between points 15 and 16 is indicative of iron precipitate deposition from the water column. The load difference suggests a reduction of 33% due to deposition; however part of the load recorded at point 16 is likely derived from downstream sources of iron in the 'West Calder' region. Monitoring at point 18 (Fe-0.055g/s), which drains the eastern side of the 'West Calder' region seems to support this interpretation as it demonstrates mine waters in the 'West Calder' region releasing iron to surface waters. Therefore the load reduction of 33% is likely to be an underestimation. The high flow load increase between points 15 and 16 of 10.47g/s indicates significant re-suspension of diffuse river bed iron sourced from Fe precipitates in close proximity to the numerous point mine water sources as well as from the low flow deposition and storage.

- Low flow iron load increase of 0.08g/s observed between point 7 and 9, correlates with the 0.08 value recorded at point 19 indicating the oil shale mining region 'Oakbank' as the likely source. There are several abandoned oil shale mines as well as significant volumes of oil shale waste in this area both of which may potentially release Fe contaminated mine waters.

- The load increase of 0.02g/s between points 10 and 11 is directly attributed to the 'Broxburn' region. This value is low, relative to the total loading along the Almond River, however is similar to the values recorded between points 2 and 3 in the coal mining region. The high flow loading increase of 1.36g/s between points 10 and 11 suggests limited but significant storage of diffuse river bed iron precipitates in the 'Broxburn' area. The Broxburn region encountered some of the most intensive exploitation of oil shale resources in the catchment, there are numerous mine sites in

the area including abandoned deep mines, reinstated opencasts and 10's of millions of tons of oil shale waste. The unmonitored tributaries, marked on Figure 4.7 in this region are likely to be heavily impacted.

- In the 'Ingliston' region two significant oil shale mines are have been observed on field visits discharging mine waters directly to the Almond River, also the mine workings are relatively shallow and are directly below the Almond River. Therefore the low flow iron loading increase of 0.09g/s between points 11 and 12 is likely to be related to these point source mine discharges as well as potentially from diffuse movement of contaminated groundwaters into the Almond River from the oil shale mines.
- It is not clear whether the iron loading increases observed in surface water quality data and attributed to the oil shale mining regions are sourced from both oil shale mines as well as oil shale bings containing processed oil shale and oil shale mine waste.

Coal and oil shale mining as both point and diffuse mine contaminant sources have been given preference as the primary source of iron in the above interpretations. The close correlation between the load increase in both iron and sulphate, as the products of pyrite oxidation at the mine site, in Figure 4.6, even with the omission of points 7,8,9 and 11 would seem to support this interpretation. However, other sources of iron which may be of influence on the observed results include urban drainage, potentially derived from anticaking agents used in road salts (Paschka et al, 1999) and sewage treatment works, as well as natural sources such as peat bogs (Fenner et al, 2001). Crucially, monitoring indicates that both coal and oil shale mining areas are significant point and diffuse sources of iron and sulphate and are observed contributing to in-stream loading in both the Almond River, Figure 4.6, and in tributaries across the catchment, Figure 4.7.

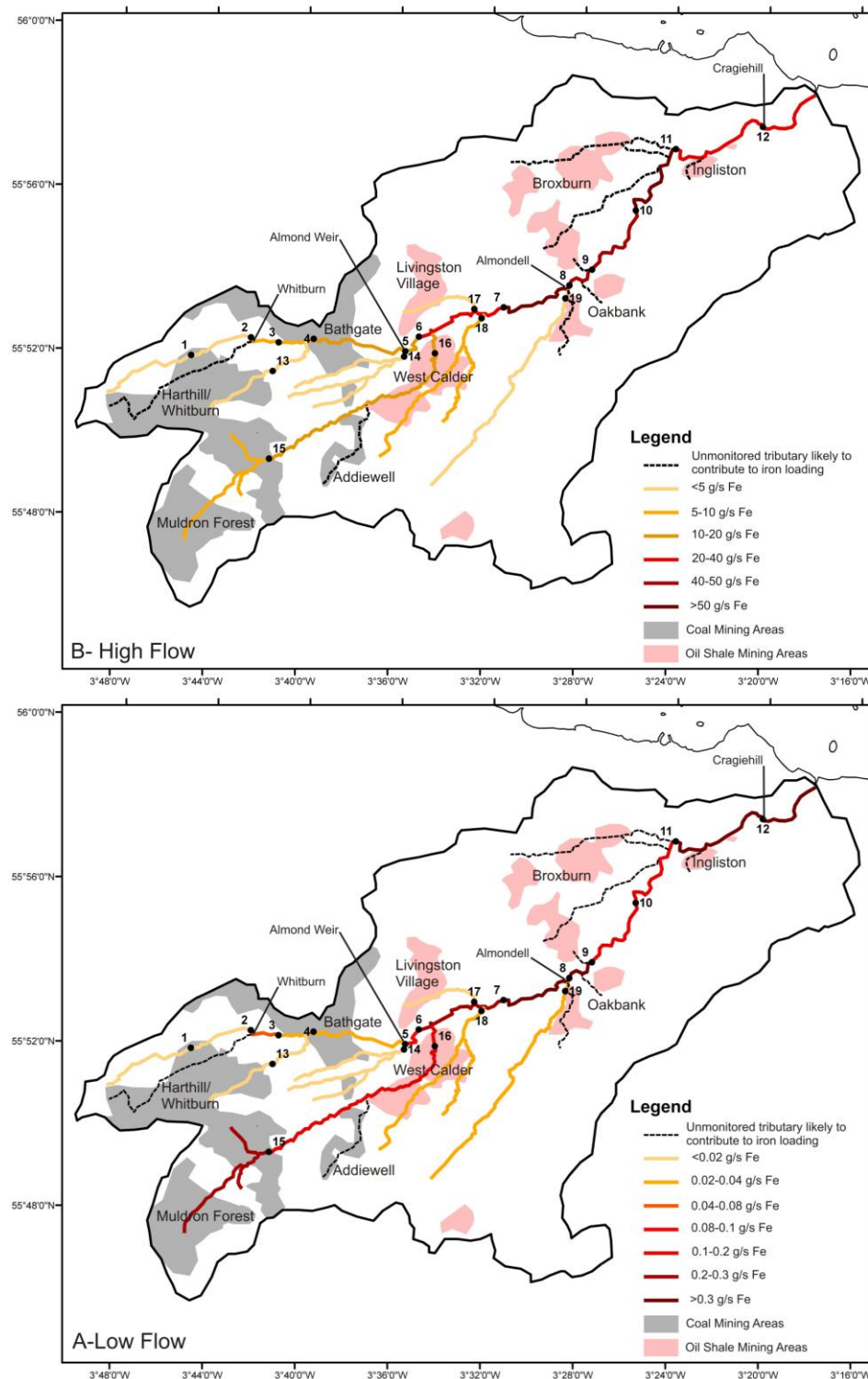


Figure 4.7 – The Almond catchment with a representation of the main mining areas and Fe load under (A) low flow and (B) high flow in monitored tributaries. Higher load values are recorded at high flow due to the re-suspension of river bed Fe precipitates, a more even distribution of load is observed at high flow in tributaries compared to low flow when area such as ‘Muldron Forest, Addiewell and West Calder dominate due to direct mine water discharge.

4.6.6 Fe trends

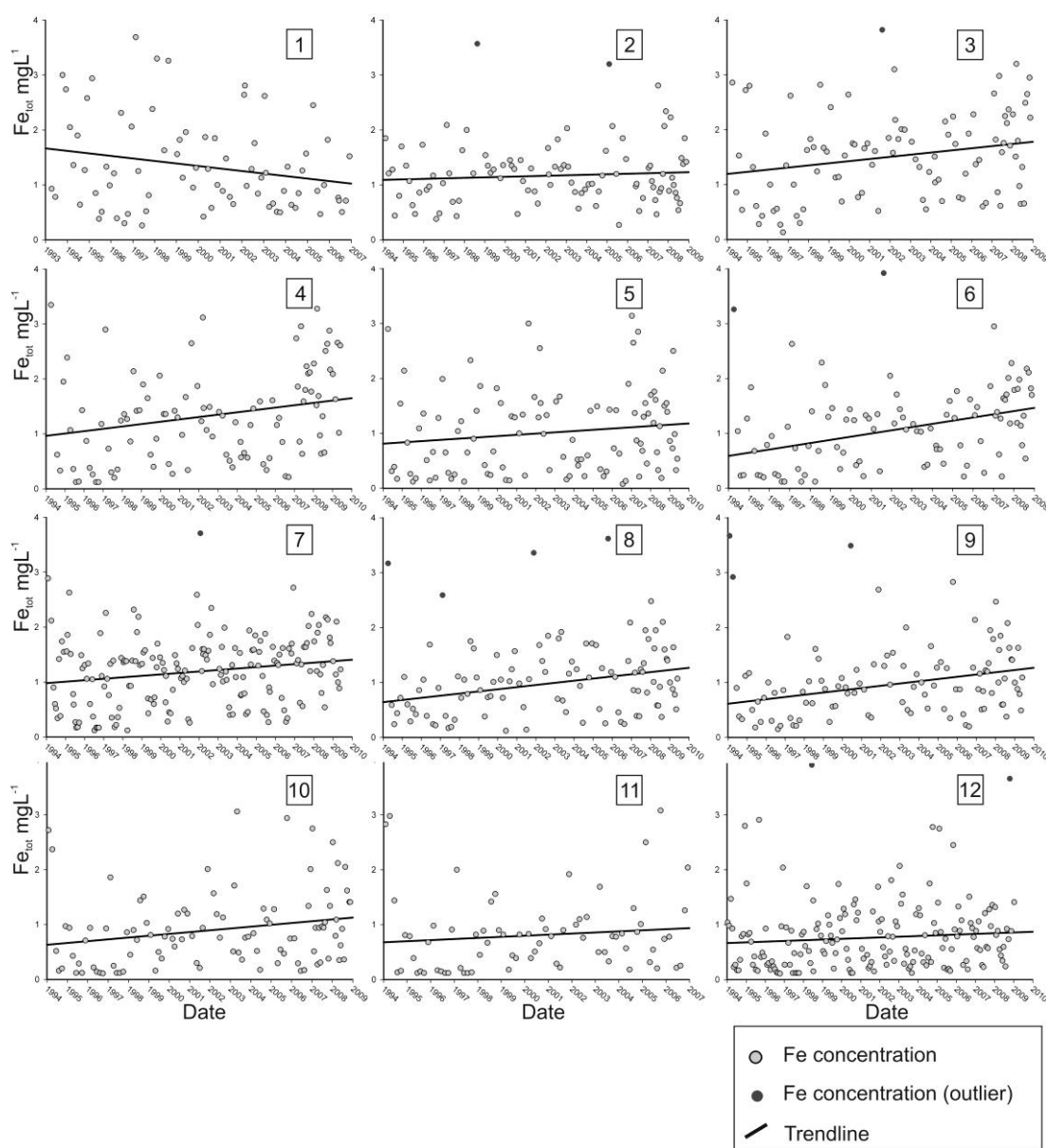


Figure 4.8 - Fe analysis data, 1994-2008, at 12 sample stations on the main Almond tributary. All the monitoring points show a gentle upward trend in Fe concentrations over the last 15 years except point 1.

Fe_{tot} concentrations in river waters at the 12 monitoring points on the main Almond tributary were considered in relation to time, over the 1994-2008 sampling period, in order to identify any potential temporal trends. Figure 4.8 displays the trend of Fe_{tot} for each of the 1-12 main Almond River tributary monitoring points. Significant scatter is observed in the data related to the flow dependence of the $Fe(OH)_3$ iron species in the surface waters, however, in generally all the monitoring points, except

Point 1, show a shallow upward trend in Fe concentration in the river waters from 1994-2008. A possible explanation for this is that although mining came to a close from 1960-1985 (depending on mined resource), it can take several decades before the main water quality impacts associated with mining occur because of extended groundwater recovery times in heavily mine areas. Indeed the main interconnected 'pond' in the Whitburn area was still in a phase of groundwater recovery in the late 1990's (Chen et al. 1999). The uncontrolled discharge of mine waters to the surface water environment even from mines not directly connected to the Whitburn 'pond' may, therefore, have been delayed due to lowered groundwater levels in the region. When discharge does occur mine waters are initially in the 'vestigial acidity' phase when contaminant release and Fe concentrations are greatest, as described by Younger (1997). This vestigial acidity phase continues for several decades, hence why an upward trend is observed in recipient surface waters. As mine waters move into the 'juvenile acidity' phase, Fe concentrations move to a lower asymptotic concentration (Younger 2000a) and a general reduction in Fe in recipient surface waters might be expected.

4.6.7 Attenuation and cumulative loading

Reductions, as well as increases, in low flow iron loading occur on the Almond River (e.g. points 3-5, points 9-10 and points 15-16), these reductions occur on river sections where the dominant process is the deposition of the $\text{Fe}(\text{OH})_3$ iron species on the river bed. Almost all river sections are likely to experience some level of iron precipitate deposition, however, where a river section receives a mine water discharge, the load reduction between monitoring points caused by deposition may be masked by the input of fresh iron from the discharge. The process of load reduction due to deposition of iron is termed attenuation (Kimball et al, 2002; Mayes et al, 2008).

The cumulative low flow iron load and attenuation can be used to give a useful quantitative measure of the relative impact of coal and oil shale mining in the catchment as a whole. Kimball et al (2002) and Mayes et al (2008) define cumulative in-stream loading as the sum of all loadings in the reaches where a positive change in

loading was measured. Cumulative in-stream attenuation is taken as the sum of the loadings in all reaches that recorded a negative change in loading. The Almond River flowing between point 1 and 12 is considered in these calculations, smaller tributaries monitored with points 13-19 are omitted; except in the determination of the amount of increase directly attributable to oil shale mining between point 6 and 7. This is calculated on the assumption that the 'West Calder' oil shale area contributes approximately the same amount of low flow load at point 16 as point 18. Therefore the load difference between point 6 and 7 attributed to oil shale mining is calculated at 0.117g/s (0.055g/s on the point 16 and point 18 tributaries and 0.007g/s on the point 17 tributary). The contribution of coal between point 6 and 7 is therefore calculated as 0.086g/s as being the difference between the oil shale load contribution and the total load increase between 6 and 7.

Omitting points 13-19 prevents a potentially unfair biased towards coal mining caused by the lack of iron monitoring on tributaries closest to oil shale mining areas, particularly in the north of the catchment, as well as problems associated with flow estimation on these tributaries. It should be noted that both the loading and attenuation values are likely to be underestimations of the true values because, as suggested previously deposition and attenuation is also possibly occurring on river sections even where a load reduction is not observed.

	Coal	Oil Shale
Cumulative Instream Loading (g/s)	0.21	0.31
Cumulative Instream Attenuation (g/s)	0.154	

Table 4.3- Cumulative low flow in-stream loading and attenuation on the main Almond tributary

Table 4.3 indicates, whilst being mindful of the limitations discussed, that coal and oil shale mining regions both significantly contribute to Fe loading on the main Almond tributary and that oil shale, at 0.31g/s, contributes more than the coal region, at 0.21g/s. The cumulative in-stream attenuation of 0.154 g/s suggests that approximately 30% of the total load discharged to the Almond River is attenuated by deposition on to the river bed. This value agrees with the load reduction value observed between 15 and 16 (of 33%), which was not included in these calculations.

As mentioned earlier, this value is likely to be much higher for the whole catchment as deposition is thought to be occurring on river beds even when a load reduction is not observed. This is supported by the observation that high flow load increases occur on the majority of monitored tributaries in the catchment (Figure 4.7B): As in order for a significant high flow load increase to occur the iron must have been previously deposited on the river bed. Also consideration of the difference in low flow and high flow load values indicates that load is increased in some cases by over 2 orders of magnitude (eg. Point 11 0.28 to 50.4g/s) indicating the significance of re-suspension of diffuse stream bed sources of iron at high flow.

If we consider all the currently monitored tributaries in the catchment it would appear coal not oil shale contributes more iron loading to the catchment rivers, however, this is an unfair comparison because of the lack of monitoring in the one of the main oil shale mined areas- 'Broxburn'. Nevertheless, the cumulative loading comparison is a useful one as it shows in a quantitative manner that iron loading and water quality is significantly impacted by mine discharge inputs from both coal and oil shale mining.

4.6.8 Major ion water chemistry

The major ion chemistry for the Almond River water is displayed in Figure 4.9; it indicates significant chemical variation in river water along the course of the river. At point 1 the river water displays a calcium dominant signature; this is likely to represent a significant component of groundwater entering the river. The Stirling and Falkirk bedrock aquifer, part of the Scottish Coal measures, which underlies this section of the river, generally displays high levels of calcium and magnesium, with local variations (O Dochartaigh et al, 2011) and is likely to be responsible for the calcium dominance. Between points 2-5, in the predominantly coal mined area, calcium, magnesium and sulphate are increasingly dominant. Beyond point 6, in the predominantly oil shale mined areas chloride and sodium become the dominant ions. This change in the dominant water signature is likely related to a change in the dominant source of waters entering the river. In the coal mined areas the major ion chemistry suggests a significant proportion of river water is likely to be sourced from

minewater discharges. Minewaters in Scotland are generally calcium, magnesium and sulphate dominant with elevated levels of iron (Younger, 2001, O Dochartaigh et al., 2011).

In the oil shale mined areas, points 6-12, where sodium and chloride become dominant, this is interpreted as being related to Na-Cl rich waters being sourced from un-burnt black oil shale and shale (blaes) discarded at oil shale waste sites and also potentially from the influence of sewage treatment from urban areas. Na-Cl type waters being discharged from shale waste have been noted elsewhere in the UK, and Germany, where they are interpreted as being sourced from the flushing of pore water brines still contained within the shaley spoil material (Banks et al. 1997, Wiggering 1993). Further investigation is required to positively identify that un-burnt oil shale waste, in the Almond, discharge Na-Cl waters, however, the concentrations in the river (Na-123mg/L, Cl-152mg/L maximum average 2005-2006) indicate that sewage treatment and urbanisation is unlikely to be the sole source of Na and Cl.

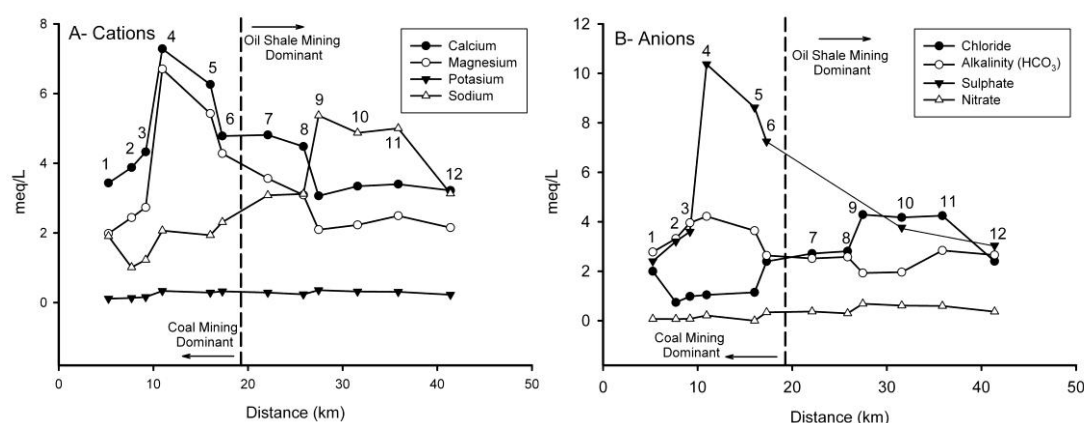


Figure 4.9 - Major ion chemistry of the Almond River waters- A-cations, B- anions (mean low flow 2005-2006). The clear change in the dominance of major ions between coal mining and oil shale mining areas is likely to be due to a difference in the composition of mine waters and mine waste leachate. In coal mining areas the dominance of Ca, Mg and SO₄ is likely due to the discharge of carbonate buffering and pyrite influences mine waters. In the oil shale area the dominance of Na and Cl is potentially related to discharges of saline pore waters from unprocessed oil shale waste and also from sewage treatment.

4.7 Conclusions and recommendations

This catchment scale study has highlighted the scale and distribution of coal and oil shale mining in the Almond River catchment. It demonstrates through correlation between potential mine site source and river contaminant loads that cumulative, point and diffuse contamination, from numerous small and large scale mine sites, within specific mining regions, cause significant and quantifiable impacts on the quality of surface water in the Almond River catchment. Of particular significance is the demonstration of a previously poorly characterised relationship between oil shale mining in Scotland and water quality impact.

Analysis of flow and concentration data identified distinct concentration flow dependence of Fe in the surface waters of the Almond related to re-suspension of diffuse river bed Fe precipitates. This is supported by water chemistry data which indicate the dominance of the solid oxidised $\text{Fe}(\text{OH})_3$ species in the Almond waters, although additional data for the year 2007-2008 also suggests a tendency for the dissolution of the $\text{Fe}(\text{OH})_3$ species to Fe^{2+} , at high flow related to a reduction in river water pH. At high flows the action of diffuse Fe precipitate re-suspension results in Fe concentrations consistently above 3mg/L and load values of up to 50g/s, several orders of magnitude higher than the load values recorded at low flow when point source mine contamination is considered to dominate. These elevated levels of Fe are undoubtedly contributing to the water quality pressures in the catchment of which sewage treatment and urban run-off are also significant, however the Fe data tentatively suggest an upward trend. Current legislation suggests that this should be addressed.

Further work on identifying and sampling discharges from both subsurface oil shale mines and mine wastes would help to further quantify the relationship between abandoned oil shale mining and reduced water quality. In addition sampling of coal discharges could help to better separate the roles of point and diffuse mine contamination sources. Investigations into the specific nature and chemistry of river bed precipitates would be needed to differentiate between diffuse Fe from mine and non-mine sources.

This study has also highlighted specific areas where monitoring could be improved to better inform the decision making process of future water quality management in the catchment. Increasing monitoring at points where Fe is already monitored in the catchment to include sulphate (points 7-9, 11, 13-19), would allow more accurate interpretations on the predominant source of Fe to be made. Fe and SO_4^{2-} monitoring on the secondary tributaries marked with a dashed line (at Broxburn, Addiewell and Harthill/Whitburn) in Figure 4.7 would also allow better characterisation and informed decision making on any required remedial efforts in oil shale mining regions.

The relationships presented here are directly applicable to other similarly mined catchments in the UK and across the World. They indicate that a whole catchment view of mine water contamination should be engaged when assessing numerous, point and diffuse mine water contamination sources. Undoubtedly, point source remediation of mine water discharges can offer significant benefit, as has already been demonstrated on some of the major mine water discharges in the Almond. However as abandoned coal and oil shale mines usually occur in clusters associated with extensive carboniferous aged deposits (in the UK) such a strategy for all sources of contamination is unreasonable, especially in catchments with up to 300 abandoned mine sites, as is the case in the Almond. A continued level of contamination release is likely to have to be tolerated in the Almond. One option for the identified high impact areas in the catchment could be regional pump and treat methods to lower groundwater levels to prevent uncontrolled mine water discharge, similar to the Durham coalfield (Younger 1995), in addition to mine waste cap and treatment methods which are becoming increasingly effective. However, adapting such regional groundwater pumping approaches in the Almond where groundwater has largely already been able to rebound could result in unforeseen complications with renewed exposure of coal measure rocks to oxygen.

Chapter 5

Mine waste: a comparative study

5.0 Chapter summary

Presented in this Chapter is an investigation into mineralogy and potential contamination associated with 4 mine waste sites chosen to represent mine waste types within the Almond River Catchment. The sites investigated were:

- an ironstone mine waste, Polkemmet Moor Ironstone Mine Waste
- a coal waste associated with a former colliery now containing a mine water treatment system, Whitrigg Colliery Mine Waste
- a second coal waste, East Benhar Mine Waste
- an oil shale waste consisting predominantly of processed waste, Hermand Oil Shale Waste

Investigations involved the recovery of rock samples at depth using a drilling rig, discharge water sampling, laboratory analysis and geochemical modelling. Results from the historical and site based investigations are presented which include site hydrogeology, bulk mineralogy, discharge water chemistry and environmental impact. Inverse geochemical models are used at each of the sites to explain the discharge water evolution and its relationship to the site history and mineralogy. Conceptual models are presented indicating the difference between the sites and potential contribution of each to water quality impacts in the catchment. The investigations indicate that pyrite and acid generating salts, AGS, (principally K-jarsoite) are the main sources of acidity and dissolved metal concentrations in discharge waters at the sites but also that carbonate and silicate weathering are significant as pH and contaminant buffers. The ironstone and one of the coal mine wastes has significant impact on surface water and potentially groundwater quality. The other coal waste site has a more limited impact similar to the oil shale waste

which is found to be depleted in pyrite due to the historic industrial processing of the waste. The use of the inverse model was considered successful with two out of the four sites investigated while the other two site model solutions are considered to offer limited insight.

5.1 Introduction

Mine waste is the most evident reminder of historic mining activity in the Almond River Catchment and arguably the same is true for most historically mined areas. The landscape in the east of the catchment is dominated by the huge orange red oil shale wastes which tower up to 95m above the surrounding area (Harvie 2005). The quantity of oil shale waste alone in West Lothian is estimated at 150 million tonnes (MacAdam et al. 1992). Coal mine waste and associated wastes such as ironstone in the west are less prominent but a number of wastes still make significant impact as large topographic features on an otherwise relatively smooth horizon.

Mineralogical, chemical and microbial action within mine waste piles can result in the discharge of significantly contaminated often acidic mine water, particularly when wastes contain sulphide minerals (Lottermoser 2010). The impact of discharge on receiving streams and groundwater is potentially a greater long term threat to water quality than discharge from flooded mines because of the continual availability of oxygen to facilitate sulphide oxidation reactions within the mine waste pile (Rees et al. 2002).

The complex and variable mining and industrial history in the catchment has produced a range of different lithology mine waste sites potentially representing a range of environmental impacts. Coal mine waste discharge waters are generally presumed to be acidic and of significant environmental concern, where as oil shale waste is assumed to be of low concern due to historic industrial processing. However, clarity is needed on these assumptions to ensure correct management of mine waste in the catchment. In this chapter a comparative study of four sites (Figure 5.1); an oil shale waste, an ironstone waste and two coal waste sites, representing the range of mine waste in the catchment is presented. Investigations at each of the sites

involved drilling to recover samples at depth, mine water discharge sampling, mineralogical analysis and geochemical modelling. The observed and potential water quality impact of each of the sites is considered in the context of mine waste across the catchment.



Figure 5.1 - OS map of West Lothian indicating the location of the four mine waste investigation sites in the Almond River Catchment shown by the red highlights.

5.2 Mine waste chemistry

The contaminant production mechanisms which operate at mine waste sites are predominantly the same as those which operate in deep flooded mines; however, the continual availability of oxygen in the surface environment allows the oxidation of sulphides, principally pyrite, to continue potentially until exhaustion. Secondly, the availability of carbonate minerals, which act as acidity buffers, is often limited at mine waste sites compared to deep flooded mines resulting in low pH strongly acidic waters.

In the Almond Catchment the significant quantity of oil shale mine wastes with altered mineralogy further complicates the processes which may be acting at the range of mine wastes investigated.

Outlined in Table 5.1 are a select number of chemical reactions which have been documented as operating at mine and mine waste sites by other studies. The table does not represent a complete set of potential reactions which may operate in mine waste and mine environments but the list has been selected to help explain the geochemistry which may operate at the mine waste sites covered in this chapter.

No	Description	Reaction	Reference
1	Pyrite Oxidation (oxygen path)	$\text{FeS}_{2(s)} + \text{H}_2\text{O} + 7/2\text{O}_{2(aq)} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$	Banwart and Malmstrom 2001
2	Ferrous iron oxidation	$2\text{Fe}^{2+} + 1/2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O}$	Banwart and Malmstrom 2001
3	Ferric iron precipitation	$\text{Fe}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_{3(s)} + 3\text{H}^+$	Banwart and Malmstrom 2001
4	Pyrite Oxidation (ferric iron path)	$14\text{Fe}^{3+} + \text{FeS}_{2(s)} + 8\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 15\text{Fe}^{2+} + 16\text{H}^+$	Banwart and Malmstrom 2001
5	Goethite Precip/Diss	$\text{Fe}^{3+}_{(aq)} + 3\text{H}_2\text{O}_{(l)} \leftrightarrow \text{FeOOH}_{(s)} + 3\text{H}^+_{(aq)}$	Lottermoser 2010
6	Siderite weathering	$\text{FeCO}_3 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$	Haney et al 2006
7	Jarosite dissolution 1	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_{6(s)} + 3\text{H}_2\text{O} \rightarrow 3\text{Fe}(\text{OH})_3 + 3\text{H}^+ + 2\text{SO}_4^{2-}$	Welch et al 2008
8	Jarosite dissolution 2	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_{6(s)} + \text{H}^+ \rightarrow \text{K}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-}_{(aq)} + 6\text{H}_2\text{O}$	Smith et al. 2006
9	Jarosite precipitation	$3\text{Fe}^{3+} + \text{M}^+ + 2\text{HSO}_4^- + 6\text{H}_2\text{O} \rightarrow \text{MFe}_3(\text{SO}_4)_2(\text{OH})_6 + 8\text{H}^+$ Where M= K^+ , Na^+ , NH_4^+ ,	Daoud and Karamanev 2006
10	Calcite weathering $6 \leq \text{pH} \leq 9$	$\text{CaCO}_{3(s)} + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$	Banwart and Malmstrom 2001
11	Calcite weathering $\text{pH} \leq 6$	$\text{CaCO}_{3(s)} + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$	Banwart and Malmstrom 2001
12	Dolomite weathering $6 \leq \text{pH} \leq 9$	$\text{CaMg}(\text{CO}_3)_{(s)} + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{Ca}^{2+} + 2\text{HCO}_3^-$	Banwart and Malmstrom 2001
13	Dolomite weathering $\text{pH} \leq 6$	$\text{CaMg}(\text{CO}_3)_{(s)} + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{Ca}^{2+} + 2\text{CO}_2 + 2\text{H}_2\text{O}$	Banwart and Malmstrom 2001
14	K-feldspar weathering (illite formation)	$6\text{KAlSi}_3\text{O}_8(s) + 4\text{H}_2\text{O}_{(l)} + 4\text{CO}_{2(g)} \rightarrow 4\text{K}^+_{(aq)} + \text{K}_2\text{Al}_4(\text{Si}_6\text{Al}_2\text{O}_{20})(\text{OH})_{4(s)} + 4\text{HCO}_3^-_{(aq)} + 12\text{SiO}_{2(aq)}$	Lottermoser 2010
15	K-feldspar weathering (kaolinite formation)	$2\text{KAlSi}_3\text{O}_8(s) + \text{H}^+ + 9\text{H}_2\text{O}_{(l)} \rightarrow 2\text{K}^+_{(aq)} + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{4(s)} + 4\text{H}_4\text{SiO}_{4(aq)}$	Lottermoser 2010
16	Albite weathering	$2\text{NaAlSi}_3\text{O}_8(s) + 2\text{H}^+_{(aq)} + 9\text{H}_2\text{O}_{(l)} \rightarrow 2\text{Na}^+_{(aq)} + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{4(s)} + 4\text{H}_4\text{SiO}_{4(aq)}$	Lottermoser 2010
17	Kaolinite dissolution	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{4(s)} + 6\text{H}^+_{(aq)} \rightarrow 2\text{Al}^{3+}_{(aq)} + 2\text{H}_4\text{SiO}_{4(aq)} + \text{H}_2\text{O}_{(l)}$	Lottermoser 2010

Table 5.1 - Selected geochemical reactions operating at mine waste sites. These are thought to be the main reaction pathways controlling the evolution of the water chemistry at the mine waste sites in the Almond.

5.3 Methods

The four sites chosen in this study were selected to represent the different mine waste deposits found within the Almond Catchment, West Lothian. A preliminary 'desk study' investigation identified the sites; this was followed by site visits to check suitability and access, following this, permissions were sought from the respective land owners to undertake intrusive site investigations. It was not considered practical to investigate one of the large oil shale sites, due to potential difficulty in gaining access to drill on such a massive structure. Instead a small easily accessible oil shale waste site was chosen to represent the larger sites.

Site 1, an ironstone waste was found to be without a land owner- the council (WLC) had no record of the site owner; the forestry commission boundary specifically excludes the site and the Coal Authority and Registers of Scotland also had no record of ownership. Site 2, a former colliery and waste site was managed by both West Lothian Council and Forestry Commission; Neil Brown the West Lothian Council contaminated land officer gave verbal and written permission by email to undertake works on the site. Site 3, a mine waste associated with the former East Benhar Colliery is owned by the Forestry Commission. Permission had to be sought via legal agreement of liability for the work through both the University and the Forestry commission. This delayed site works by over a month compared to the other sites and drillers had to be demobilised and then remobilised. Site 4 was owned by a local farmer; permission was given by an informal telephone conversation prior to the work being undertaken. (Correspondence and permissions to undertake the works where necessary can be found in Appendix B)

5.3.1 Site investigation

The intrusive site works phase of the investigations were undertaken in September and October 2010, and consisted primarily of 1) recovering solid mine waste samples at depth from a number of locations 2) installing sample locations with standpipes and 3) sampling direct discharges and surface waters in close proximity to the sites.

Mine waste samples were recovered from cores extracted at depth using a tracked windowless sampler or handheld window sampler at between 8 to 10 locations at each of the sites. Samples were recovered , every 20 to 50 cm, generally in the upper 4 meters of the waste but in some cases up to a maximum depth of 7m bgl (below ground level). Samples were immediately bagged and then placed into refrigerated storage to await mineralogical analysis by Quantitative X-Ray Diffraction, QXRD. Approximately half of the sampled locations were utilised for the installation of 35mm diameter standpipes which were surrounded by graded pea gravel and sealed at the top with bentonite (Figure 5.2). The stand pipes were used to check water levels at the sites and to recover water samples where possible.



Figure 5.2 - Site investigation photos. **Left-** sampling rig used to recover mine waste samples at depth and to facilitate borehole construction, **Top Right-** sampling equipment and borehole construction, **Bottom Right-** borehole covering following installation.

5.3.2 Water sampling

Mine waste water discharges, recipient and close proximity streams and rivers were sampled. Waters were analysed on site for pH, Eh, conductivity and temperature using either Hach or Mettler Toledo portable probes which were calibrated daily and checked regularly particularly when moving between different water types. No issue with drift or inaccuracy in meter readings was observed. Bicarbonate alkalinity, as CaCO_3 , was also recorded at the time of sampling using a portable titration kit. Titrations were made in triplicate and average readings calculated to ensure precision. Bicarbonate alkalinity as HCO_3^- was calculated by multiplying the averaged reading by 1.22. Samples of the water, filtered using $0.45\mu\text{m}$ disposable filters, were collected in 30 or 60ml nalgene plastic analysis bottles and acidified to 1% v/v with Aristar HNO_3 on site. The samples were placed in refrigeration and sent to the BGS labs in Keyworth for analysis of major ions and trace elements.

Presented also, in the case of Site 1, from an earlier investigation, are chemical analysis results of composite surface samples. These samples were recovered with a trowel and bucket from the top 50cm at 30 evenly spaced locations across the waste site according to a method outlined by Smith et al. (2000).

5.3.3 Mineralogical and chemical analysis

The mine waste samples were allowed to air dry for a minimum of 48hours prior to being sieved using a 2mm sieve. In general only the $<2\text{mm}$ fraction was selected for analysis as it is considered to have the greatest leachate potential (e.g. Price and Kwong, 1997). When the above 2mm fraction or a fragment of rock was also selected for analysis they were generally crushed to facilitate the analysis. The sieved or crushed sample was then placed into a tungsten-carbide rotary mill for between 30 seconds and 2 minutes, depending upon the sample type, to obtain a pulverised homogenised powdered sample. A sub-sample of the powder was then suspended in analytical grade alcohol (chosen instead of water due to the water sensitivity of mine waste minerals) and placed in a McCrone micronising mill for 12 minutes to obtain a slurry which is then sprayed through a vessel at $100\text{-}120^\circ\text{C}$. This produces a randomly orientated powder which is mounted on a plate ready for X-Ray

Diffraction analysis. The plate is loaded into the Bruker D8-Advance X-ray Diffractometer in the School of GeoSciences, University of Edinburgh which employs a 2-theta configuration in which the X-rays are generated by a Cu-anode x-ray tube operating at 40KV and a tube current of 40mA. The diffracted x-rays were detected using a Sol-X energy dispersive detector that allows only the characteristic Cu K-alpha radiation to be analysed thus filtering out any fluorescent x-rays generated in the sample and giving a very low background count rates. The samples were scanned from 2 to 60 degrees two theta at a scan rate of 0.01°/second and the resultant diffractograms compared with the 2011 issue of the International Centre for Diffraction Data (ICDD) diffractogram database library using the EVA analysis package. This procedure typically gives a detection limit for crystalline phases of approximately 1 wt.% (it should be noted, however, that amorphous materials do not produce diffraction patterns and thus XRD will only detect the mineral components present in a sample).

5.3.4 Rietveld analysis

To quantify the amounts of the minerals present in the samples the diffractograms were imported into the TOPAS analysis software for Rietveld analysis. The procedure is as follows. The mineral assemblage occurring in the sample is first identified by comparison of the peak heights and positions with those in the powder diffraction database (as described above). The TOPAS program then uses an iterative routine in which a 'model' diffraction pattern is calculated based first on an initial estimated mineral assemblage. This is then compared to the diffractogram obtained from the sample and the amounts of the minerals in the estimated assemblage modified to reduce the differences between the model and observed pattern. The next iterative cycle is then begun and a new model pattern generated. After about 100 iterations the model pattern converges on the observed pattern thus revealing the wt.% amounts of the solid phase minerals present. Amorphous phases are excluded, which could be a potential source of error particularly in samples with high abundances of coal. This needs to be considered when assessing the results of XRD analysis from mine waste sites. The detection limits of this technique are similar to the initial diffractograms at ~1 wt%. The QXRD results are summarised in tables in

the following sections for each of the sites investigated. The abundances of minerals have been quoted where their levels rise above 0.1 wt % despite the effective detection limits being 1 wt.%. This is to give an indication of the potential for mineral contents below 1 wt% however all interpretations of mine waste chemistry and environmental impact are made in light of the effective detection limit of 1 wt%. (Technical account of the QXRD method originally provided by Dr. Nic Odling, Senior Technical Officer, University of Edinburgh). The QXRD analysis is summarised in for each site in this chapter, raw analysis results are provided in Appendix D.

5.3.5 Accuracy and repeatability

The results of the XRD analysis within this study are principally used to identify the bulk mineralogical phase assemblages of the analysed samples. These phase assemblages are used as inputs to geochemical models to give an explanation of the observed discharge water chemistry. The absolute quantity of each mineral phase does not affect the results of the investigation in this regard, however, in order to give an indication of the accuracy and repeatability of the method used a synthetic sample of known composition was analysed using the method described above. Furthermore, a sample from site 1, which was identified as containing both pyrite and k-jarosite (being the main potential sources of acidity at each of the site) was selected and repeatedly analysed on the XRD eight times to give an indication of the repeatability of the method.

	Analysed	Known	Accuracy(%)
Quartz + Orthoclase	11.8	15	-21
Pyrite	4.48	5	-10
Illite	9.3	10	-7
Kaolinite	11.7	10	17
Muscovite	26.87	25	7
Dickite	35.7	35	2
Total	99.85	100	-0.15

Table 5.2 - QXRD analysis (wt%) of synthetic sample. The sample was created using a mechanical mix of known mineralogy, the sample was then analysed to give an indication of the accuracy the XRD method for differing mineral types.

	1	2	3	4	5a	5b	5c	5d	Av.	Max.	Min.	Range
Quartz	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.1
Calcite	0.62	0.08	0	0.43	0.26	1.5	0.78	0.8	0.6	1.5	0.0	1.5
Dolomite	0.06	0.23	0	0.92	0.47	0.8	0.09	0.93	0.4	0.9	0.0	0.9
Pyrite	1.36	1.16	1.48	1.12	1.2	1.3	1.24	1.29	1.3	1.5	1.1	0.4
Illite	35	38	30	32	36	34	35	32	34.0	38.0	30.0	8.0
Kaolinite	11.2	11.7	10.6	10.6	10.9	13	11.9	11.6	11.4	13.0	10.6	2.4
Siderite	0.23	0.13	0.13	0	0.3	0.3	0	0.52	0.2	0.5	0.0	0.5
Microcline	5.6	3.8	3.4	2.6	4	3.4	3.5	4	3.8	5.6	2.6	3.0
Orthoclase	1.6	0.9	2.5	2.3	1.25	1.4	0.64	1.1	1.5	2.5	0.6	1.9
Jarosite	3.1	3.3	5.2	4.2	3.7	2.4	2.6	2.9	3.4	5.2	2.4	2.8
Albite	0.47	0.08	0.5	0	0.98	0	0	0.62	0.3	1.0	0.0	1.0
Muscovite	7.6	8.9	9.6	11	7.3	10.6	12.1	11.8	9.9	12.1	7.3	4.8
Dickite	32	30	35	32.5	32.1	30	30.4	30.8	31.6	35.0	30.0	5.0
Goethite	1	1.41	1.81	1.73	1.5	1.3	1.72	1.58	1.5	1.8	1.0	0.8

Table 5.3 - QXRD analysis (wt%) of repeat sample. A sample from Site 1 was repeatedly run on the XRD to give an indication of repeatability of the QXRD analysis.

Table 5.2 indicates that the analysis on the synthetic sample analysis result falls within what would be considered to be an accurate XRD analysis method, as the analysed result, in general, falls within 3wt% of the known value (Calvert et al. 1989). The accuracy of the Rietveld method, as conducted in the University of Edinburgh, has also been demonstrated by other studies (e.g. Lu 2008).

Table 5.3 indicates that the QXRD method is repeatable; however, the greatest range of analysis results were recorded on the clay minerals such as illite, 8.0wt%, muscovite, 4.8wt% and dickite, 5.0wt %. This is likely to be related to the effects of preferred orientation associated with these sheet silicate minerals.

The results of the accuracy and repeatability measures employed indicate that there are likely to be some, relatively small, errors in analysis associated with the relative abundance of clay mineralogy at the investigation sites described in the following sections. In general, however, it is considered that QXRD analysis accuracy and repeatability is adequate for the purposes of this study, particularly as the phase assemblages, not the absolute abundances, are used in the site geochemical models.

5.3.6 Water analysis

Water samples collected were sent to the British Geological Survey (BGS) UKAS accredited Analytical Geochemistry Labs in Keyworth. Major and trace elements

were determined by inductively coupled plasma mass spectroscopy, ICP-MS. Selected anions (Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , Br^- , F^- , HPO_4^{2-}) were determined using ion chromatography and pH and alkalinity, in addition to field analysis or where field analysis could not be undertaken, were determined by potentiometric titration. The analysis reports provided by the laboratory can be found in Appendix C.

5.3.6.1 Balances

Sampling of discharge waters, groundwaters and river waters associated with the intrusive site investigations of mine wastes was undertaken according to standard methods (e.g. Ó Dochartaigh et al. 2011) ensuring samples were filtered and acidified on site, placed into a cooler box and then refrigerated within 12 hours ready to be sent to BGS laboratories for analysis. In a number of cases the ionic balances of samples were found to fall outside of the standard $\pm 5\%$ ionic balance required for a ‘good’ groundwater analysis. This is thought to be related to the complex geochemistry operating at the mine waste sites where waters are emerging from the waste pile causing rapid changes in temperature, redox and oxygen availability resulting in precipitation, particularly associated with Fe and Mn, and speciation changes in dissolved elements. Most groundwater samples to which the 5% balance rule is applied are recovered from well developed boreholes in ‘natural’ aquifers where waters are in equilibrium with aquifer materials. The complex and relatively rapid evolution of water chemistry in mine waste environments produces discharge waters which may be in disequilibrium, particularly when obtaining a sample at the exact point of emergence can be difficult or impossible.

Cornin and Furey (1998) provides guidance on interpreting water analysis and states that ‘*ionic balance error should be less than 15% for leachate and 5% for groundwater*’. Poor ionic balances are a common feature of mine waters and are often associated with high Fe concentrations leading to the formation of Fe complexes causing difficulties in analysis and titrations (Younger 1995). All the ionic balances for mine water discharges and associated river samples, which are effectively leachate samples as opposed to true groundwater samples and fall, within $\pm 15\%$, most fall within $\pm 10\%$. However, in order to increase confidence in

interpreting the chemistry of the mine water environments a number of discharge samples were re-sampled with the intention to produce samples with improved ionic balances. The dates of sampling and the ionic balances are reported with all of the whole water chemistry analysis presented in the ‘Sampled Waters’ section for each of the sites.

Where water was recovered from borehole installations at the sites only selected chemical analysis have been presented, namely Fe and SO₄, this again is because of poor ionic balances. Here though the problems are thought to be related to 1) the potential for disequilibrium as the water is rapidly evolving along its flow path in the waste 2) issues with the basic construction of small diameter piezometers and their poor development as a groundwater sampling points and 3) in the case of Sites 1 & 3 surrounding boreholes are installed into peat which show high carbon contents thought to impact the speciation chemistry of dissolved ions.

5.3.6.2 Speciation modelling

The principal discharge samples as well as selected downstream samples were input using the PHREEQC interface (Parkhurst and Appelo, 1999) into the WATEQ4F code (Ball and Nordstrom, 1991) in order to consider the speciation of dissolved constituents and the saturation index ($\log(IAP/K_T)$) of selected AMD associated mineral phases. As stated by Younger (1995) the WATEQ4F ‘*code is particularly suited for modelling minewater chemistry as the latest version of the database (Ball and Nordstrom 1991) incorporates findings of many years of research into inorganic AMD chemistry undertaken by Nordstrom (1982)*’. The saturation index for AMD minerals are presented with the whole water chemistry data for selected analysis under the ‘Sampled Waters’ section for each of the sites. In general goethite, jarosite and iron oxyhydroxides are presented, jarosite-ss is presented as the general form for a number of different jarosite family salts- potassium jarosite (K-jarosite), natrojarosite (Na-jarosite) and hydronium-jarosite (H-jarosite).

5.3.7 Modelling discharge chemistry evolution

The model code PHREEQC was used to identify the principal hydro-geochemical processes which result in the discharge water chemistry at each of the minewaste sites investigated.

The ‘**INVERSE-MODELING**’ keyword in PHREEQC requires the definition of two solutions using the ‘**-solutions**’ identifier, one *initial* rainwater composition and one *final* discharge composition. The probable mineralogical phases, determined here through QXRD analysis, and potential gaseous phases which are present along the evolutionary pathway between the two solutions are also defined using the ‘**-phases**’ identifier. The inverse modelling function determines sets of mole transfers of phases that account for the changes in the water chemistry between the *initial* and *final* water composition (Parkhurst and Appelo, 1999).

The model also requires the definition of uncertainty to be used for each of the elements present in the solution. The ‘global uncertainty’ for each of the models was set initially at 0.05, this means that each element in both the initial and final solution is allowed to vary by up to plus or minus 5 percent in order to produce the model solutions. This level of uncertainty is appropriate due to the difficulty in obtaining below 5% analytical balances in the mine waters. The global uncertainty can be overridden by using the ‘**-balances**’ identifier to give an individual element a differing uncertainty value. As chloride, nitrate and manganese are not present in any of the phases determined by XRD analysis they were given an uncertainty value of 1. This effectively excludes them from the inverse model and the solution produced will not account for the difference in concentration of these elements between the *initial* and *final* solutions defined. Although this will produce a solution which does not fully explain the chemical evolution of the discharge water, the solution should still offer an explanation, based on a chemical mass balance, for the dominant geochemical processes operating at the sites. Other conditions applied to the model include the option to allow a mineral phase to only ‘dissolve’ or ‘precipitate’. This does not force the inclusion of a mineral; a solution with neither precipitation nor dissolution of that

mineral phase can be returned. But no solutions where the mineral dissolves will be returned if the option to only precipitate has been included; the reverse is true.

In each of the models presented here the option to only dissolve was applied to calcite, dolomite, K-jarosite, pyrite, K-feldspar and K-mica (muscovite), when present in the mine waste phase assemblage. Where the pH of mine waters was low, namely at Site 1, the option to only dissolve siderite was also included as the formation of siderite at low pH is considered to be unlikely. The option to only precipitate goethite was also included as a condition. These model constraints are considered logical in view of the prevailing geochemical conditions which operate at mine waste sites.

The use of inverse geochemical modelling has been demonstrated in a number of studies (Herbert 1994, Lyons & Bird 1995, Berk & Wisotzky 1995, Glynn & Brown 1996, Soulsby et al. 1998) to model water chemistry evolution and specifically by Chen et al. (1999) to model the evolution of mine water at the Polkemmet Mine, also in the Almond River Catchment. The inverse approach used here is similar, although QXRD identified mineralogical assemblages are used as apposed to assumed assemblages, based on geological knowledge. Also Chen et al. (1999) use NETPATH (Plummer et al 1994) in their inverse calculation which unlike PHREEQC does not incorporate consideration of analytical error. The inverse model itself is considered a robust tool to identify the main geochemical processes operating at the sites presented in this study, however, one possible source of error and uncertainty is the aforementioned problem that some of the recovered samples showed poor ionic balances potentially related to the mine waste discharges waters being in dis-equilibrium. If this is the case this could result in errors in the speciation model used on the samples, prior to the inverse model, as this model assumes samples are in equilibrium. This should be born in mind when interpreting results, particularly for samples with poor ionic balances. As mentioned previously, some sites were re-sampled to try to achieve improved ionic balances and these samples should always be given preference over the less good samples within the geochemical models.

5.3.7.1 Rainwater composition

In all the solutions presented for inverse calculations at each of the sites the initial solution was defined as the rainwater composition at the Sourhope monitoring station in SE Scotland (Longitude: -2.21050834 Latitude: 55.48980713). The data was recovered from the 'UK Environmental Change Network' website using the data discovery portal and is displayed in Table 5.4 . The sample electron activity, pe, value was calculated in PHREEQC using a nitrate species redox couple.

Loaction	Date	pH	pe	Ca	Mg	Na	K	Alk as CaCO ₃	Cl ⁻	SO ₄ ²⁻ as S	NO ₃ ⁻ as N	Balance (phreeqC)
Sourhope	Oct-10	5.219	9.2	0.109	0.1295	1.228	0.021	0	1.5452	0.2004	0.1679	11.83

Table 5.4 - Sourhope Rainwater Composition January 2011- units in mg l⁻¹, except pH and pe. Balance as a percentage (UK-ECN data)

5.4 Site 1 – Polkemmet moor ironstone waste

Site 1 is located on Polkemmet Moor at NS 9150 6260, approximately 2.5km NNW of the town of Fauldhouse in West Lothian (Figure 5.1). It can be accessed immediately to the east of Harthill Road between Fauldhouse and Harthill. The abandoned Polkemmet colliery is located to the north east of the site as is the town of Whitburn. To the south west is the town of Shotts.

5.4.1 Site history

The ‘Polkemmet Moor Ironstone’ waste first appears on the 1st Revision Lanarkshire Sheet county series 1:2500 OS map surveyed in 1896 (Figure 5.3). There are several ‘old shafts’ on the map close to the site from which the waste may have originated. Otherwise the waste may have been transport from a mine to its current location; the mineral railway arrangement suggests the waste could have originated from either the ‘Benhar Colliery’, the ‘Fallahill Colliery (Pit No1, 3 and 4)’, to the south, or one of the several small ‘West Benhar’ associated mine sites, to the west. Initial observations at the site indicate the waste to be a predominantly grey clayey ‘argillaceous’ mudstone/shale containing orange red rounded nodules.



Figure 5.3 - Site1-Polkemmet Moor Ironstone Waste- Lanarkshire Sheet county series 1:2500, showing the extent of the site in the centre, associated mine shafts from which the ironstone waste may have originated. Alternatively the waste may have originated from more distal sites having been transported via the mineral railways also identified on the map.

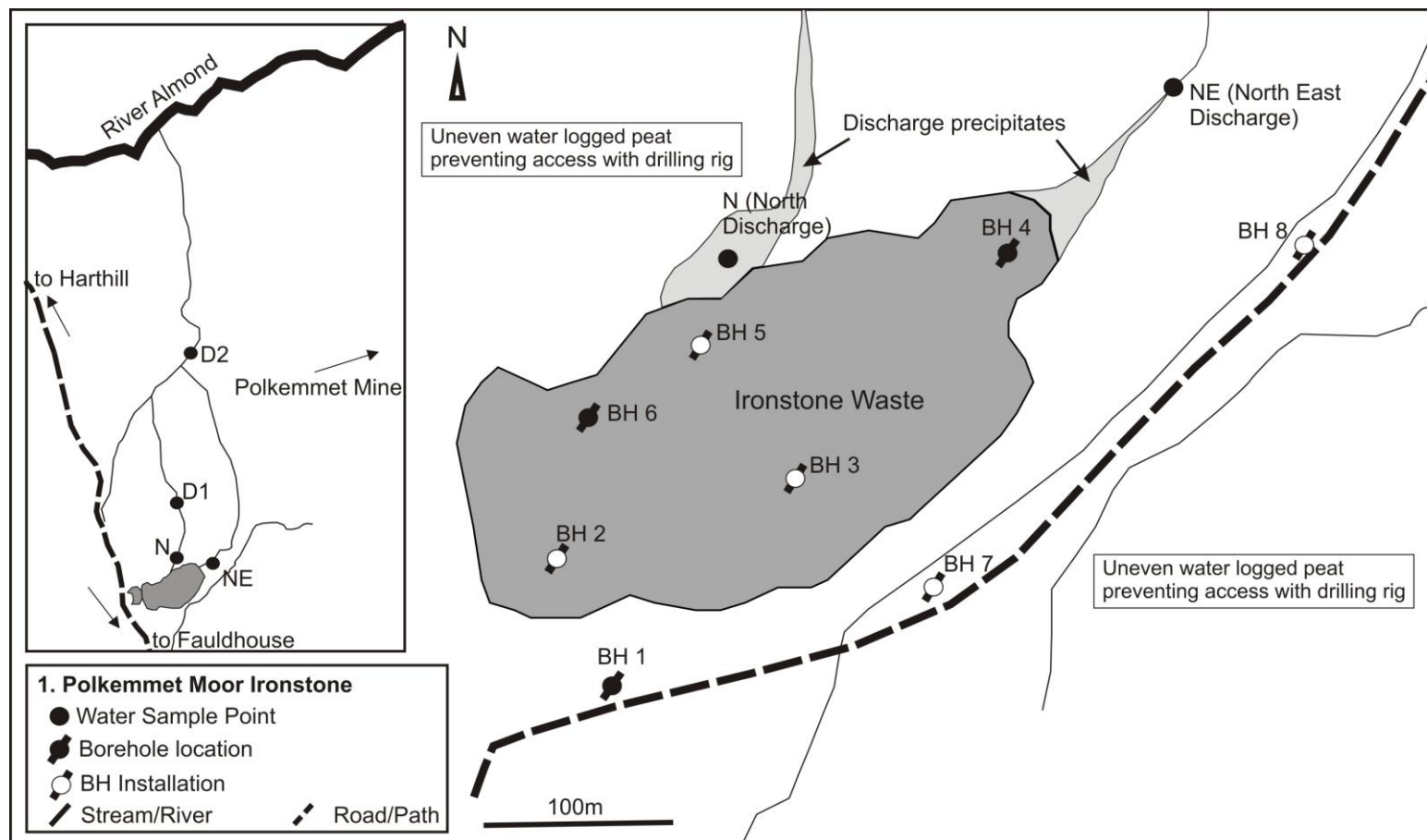


Figure 5.4 - Site 1- Site investigation works plan showing the central ironstone waste pile (dark grey) and two separate (N&NE) discharges with associated areas of precipitate mineral formation (light grey). Five boreholes (BH2-6) were excavated into the waste pile, three boreholes (BH1, 7&8) were excavated into peat to the immediate south and east of the site, ground conditions in the surrounding areas prevented safe access with the drilling rig.

5.4.2 Ground conditions

Site overview

The site comprises approximately 32,000m² of grey clayey mudstone/shale mine waste, 3-5m in height, with two principal mine water discharge streams, a consistent north discharge (N) and a less consistent north eastern discharge (NE) (Figure 5.4). Variable discharge volume was observed at both discharge streams during site visits (Figure 5.6). Historic maps indicate that there was a marshy stream at the site prior to the deposition of the waste; the present day discharges may incorporate waters from off site however no other significant surface waters have been observed at the site. The two discharges flow north through a wooded area, maintained by the Forestry Commission, and converge approximately 800-900m downstream, on their respective channels, adjacent to 'Greenrigg' farmhouse. Following convergence the discharge stream continues north for approximately 1000m before entering the River Almond on its south bank close to the eastern edge of the town of Harthill.

The N and NE discharges show sizeable areas of precipitate and hardpan formation associated with the wash down of mine waste from the pile bound together by the precipitation of mineral salts from the discharge waters (Figure 5.5). The surface of these hardpan areas varies from orange, red and yellow to green indicating goethite and jarosite mineral formation. As the discharges flow through the adjacent forested area to the north, orangey yellow clayey precipitates are observed on either side of the streams, formed at high flow when the stream width is increased. Where the N and NE discharges converge, close to 'Greenrigg Farm', stream bed orange ochre deposits are observed which extend along the length of the stream to the point of discharge into the River Almond.



Figure 5.5 - Photographs showing hardpan and precipitate formation on NE (left) and N (right) discharges. The orange colouration of sediment and precipitate minerals indicating goethite, while the distinct green grey colouration around discharge waters on the N discharge indicates K-jarosite precipitate minerals.

Intrusive site works

Intrusive site work involved sampling and borehole installation formed using a handheld window sample rig. A tracked windowless sample rig was not used because of a) poor site access and b) high angle mine waste flanks. Eight intrusive boreholes were drilled, five in the waste (BH2-6) of which three (BH2, 3 & 5) were installed with smaller diameter piezometers, and three (BH1, 7&8) to the south and south east of which two (BH7 & 8) were installed with piezometers. No boreholes were undertaken to the north or west of the site because the ground conditions made access unsafe (Figure 5.4).

Boreholes in the waste were drilled to depths between 3 and 3.5mbgl, mine waste was recovered every 0.25-0.5m. The recovered waste varied from 1) layered weathered clayey sandy gravel of mudstone and shale showing patches and layers of orange, yellow and green oxidation to 2) yellow and grey silty clay layers and 3) occasionally layers of gravels and boulders of mudstone and shale. The upper 0.5m of the waste generally showed a more clay dominant structure likely related to increased weathering at the surface.

Boreholes (BH7 & 8) formed into the surrounding areas revealed a brown clayey poorly decomposed peat approximately 3m thick with a water strike at or close to surface. Below the peat, grey and orange silty clay was encountered (Borehole logs are provided in Appendix B). These observations are consistent with the superficial geology on the 1:50,000 British Geological Survey (BGS) for the area which shows peat on Polkemmet Moor surrounded (underlain) by Devensian till deposits. BH1 recorded made ground deposits of sand, gravel and clinker likely related to the historic mineral railway which ran past the south side of the site.

The solid geology below the site on BGS maps is shown to be Scottish Middle Coal Measures underlain by Scottish Lower Coal Measures.

North discharge flow variation



Figure 5.6 - Variability in flow at the North Discharge- greater flow volume was observed on the north discharge during initial mine waste catchment sampling work in 2009 (left) compared to intrusive site investigation work in 2010 (right)

On 23/11/2009 (Figure 5.6, left) considerably more flow was observed from the N discharge than on 21/10/2010 (Figure 5.6, right), due to increased rainfall in winter months causing increased water infiltration and discharge volume. As can be seen in Figure 5.6 the nature of the discharge stream made it unfeasible to try to make accurate flow measurements of the site discharge volume.

Groundwater

Borehole installations in and around the mine waste pile at Site 1 were monitored on 2/11/2010. No groundwater strike was recorded in any of the boreholes within the waste pile (BH2, 3 & 5). Groundwater in the BH 7 & 8, installed in the peat, was recorded at just below the surface level at 0.1mbgl (Table 5.5).

Borehole	GW Strike (mbgl)	Base (mbgl)
BH2	No GW strike	3.5
BH3	No GW strike	3.5
BH5	No GW strike	3.0
BH7	0.1	3.5
BH8	0.1	3.5

Table 5.5 – Groundwater level monitoring from borehole installations at Site 1 on the 2/11/2010. Borehole positions are shown on Figure 5.3

5.4.3 Mineralogy

The results of QXRD analysis on the 24 samples recovered from BH 2, 3 and 5 are presented in Table 5.6. The analysis revealed that the waste consists predominantly of clay and sheet silicate minerals, dickite, illite, kaolinite and muscovite with minor fractions of quartz, feldspars, carbonates- calcite, dolomite and siderite, pyrite and precipitate minerals jarosite, goethite and lepidocrocite. K-jarosite and goethite detected ubiquitous in the sampled waste with median values of ~2wt% and ~1.9wt% respectively, the pyrite content is variable but in places reaches up to ~7wt%. Analysis undertaken on a sample of one of the nodular ironstones recovered from the surface of the waste site revealed it to be dominantly siderite (FeCO_3) with minor fractions of pyrite (FeS_2) and goethite (FeOOH) (Figure 5.8B).

Mineral Phase	Formula	n	Max	Median	Min
Quartz	SiO_2	24	4.3	0.8	0.0
Microcline	KAlSi_3O_8	24	7.4	4.5	0.3
Albite	$\text{NaAlSi}_3\text{O}_8$	24	1.8	0.3	0.0
Orthoclase	KAlSi_3O_8	24	1.2	0.2	0.0
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$				
Dickite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	24	62.9	44.0	28.4
Illite	$\text{K}_{1.5-1.0}\text{Al}_4[\text{Si}_{6.5-7.0}\text{Al}_{1.5-1.0}\text{O}_{20}](\text{OH})_4$	22	21.9	10.1	5.1
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	24	22.4	15.6	1.4
Muscovite	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	24	18.8	13.8	8.2
Calcite	CaCO_3	23	1.1	0.6	0.1
Dolomite	$(\text{CaMg})(\text{CO}_3)_2$	23	0.9	0.5	0.0
Siderite	FeCO_3	20	5.0	0.4	0.0
Pyrite	FeS_2	24	7.5	0.4	0.1
Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	24	3.5	2.1	0.9
Goethite	FeOOH	24	12.2	1.9	1.1
Lepidocrocite	$\gamma\text{-FeO}(\text{OH})$	1	1.5		

Table 5.6 - QXRD mineralogical analysis results (in wt %) returned by the reitveld analysis from samples recovered at Site 1. Analysis identified acidic mine drainage associated minerals, pyrite and jarosite, at environmentally significant abundance and low abundance of carbonate buffering minerals calcite and dolomite.

Iron and sulphate minerals

Pyrite and K-jarosite XRD stick patterns were positively identified in the waste traces (Figure 5.8A), QXRD found them to vary in wt% at different BH locations and mine waste horizons. Figure 5.7 displays the vertical profile of pyrite and K-jarosite wt% in three boreholes. The pyrite content in each is variable ranging from below 1wt% to 7wt% at 1.4mbgl in BH2. The K-jarosite content is more consistent, generally around 1-2 wt% but in some horizons reaching up to 3-4wt%.

An interesting feature of the depth profiles displayed in Figure 5.7 is the relative relationship between pyrite and jarosite content. Where there is an increase in K-jarosite content there is generally a corresponding reduction in pyrite content. Caution must be taken in interpreting such observations as the profiles do not represent continuous profiles but discrete sampling points.

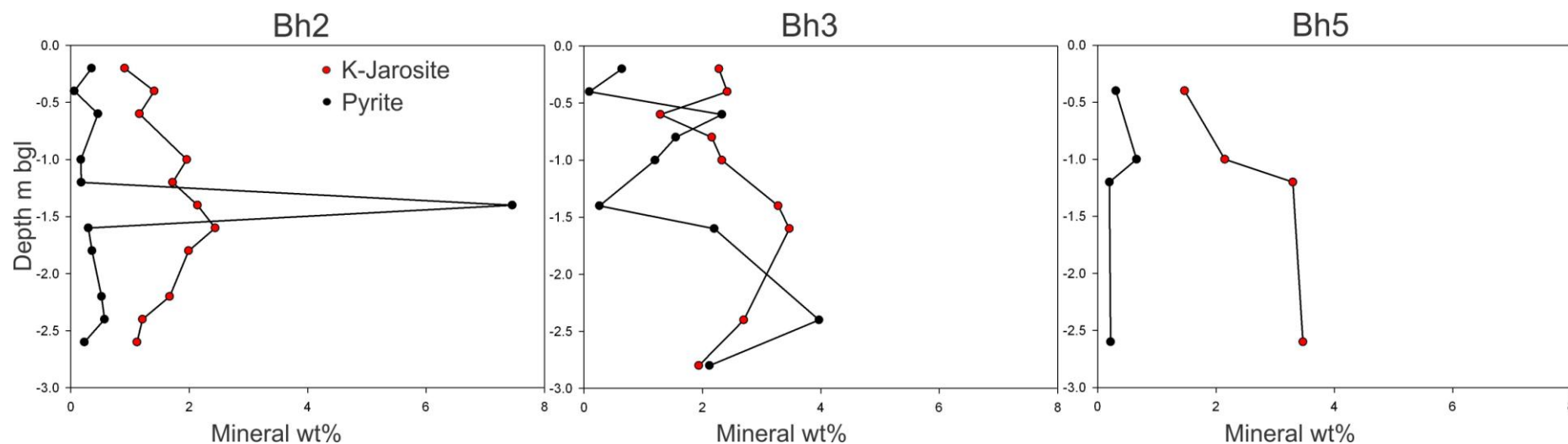


Figure 5.7 - Depth profiles of pyrite and K-jarosite abundance analysed via QXRD reitveld analysis on samples recovered from boreholes at Site 1. The lines shown the indicative change in mineral abundance identified via discrete sampling at depth from BHs 2, 3 & 5 drilled into the ironstone waste pile.

Carbonates and silicates

Calcite and dolomite XRD stick patterns were visually identified in only a select number of the 24 traces returned for the site. However, both were included as phases in assemblages for all of the traces in the Rietveld mineralogical analysis because of their importance as potential acidity buffers in mine waste environments. This, produced quantitative wt % for calcite of below 1wt% except in two samples, one in BH3 at 1.08 wt% and one in BH5 at 1.06 wt%. Dolomite was analysed at below 1wt% in all samples. As the effective QXRD detection limit is 1wt% the confidence placed in the median values of 0.64 wt% for calcite, and 0.45wt% for dolomite is low although they are likely to be fair estimates.

Siderite is a Fe carbonate (FeCO_3) and was identified in BH2, 3&5 up to 4.95 wt%, and in ironstone nodules as the dominant mineral phase. Microcline was identified in the majority of the analysed samples with a median value of 4.5wt%; albite and orthoclase were also identified in a number of samples at above 1wt%. Kaolinite and muscovite were identified at high relative abundances with median values of 15.5 and 13.8wt% respectively.

Precipitates

Two areas of precipitate and sediment hardpan accumulation were observed at the site related to the two principal discharge locations. The majority of the accumulation at these locations were small fragments of the waste washed down from the surface of the waste pile, probably during periods of high flow and rainfall, which are bound by orange, red and green mineral precipitate ‘crusts’. QXRD analysis (Figure 5.8C) of the green mineral precipitates identified the mineral as Na-jarosite which differs from the K-jarosite identified in the majority of the waste pile. Na-jarosite forms in low pH waters containing Fe and SO_4 , reaction 9, Table 5.1.

Downstream from the north discharge, approximately 100m, orangey ochre was observed on the exposed stream bed on either side of the present discharge stream. QXRD analysis produced an amorphous trace indicating the substance is likely to be a hydrated iron oxide ochre (Reaction 3, Table 5.1).

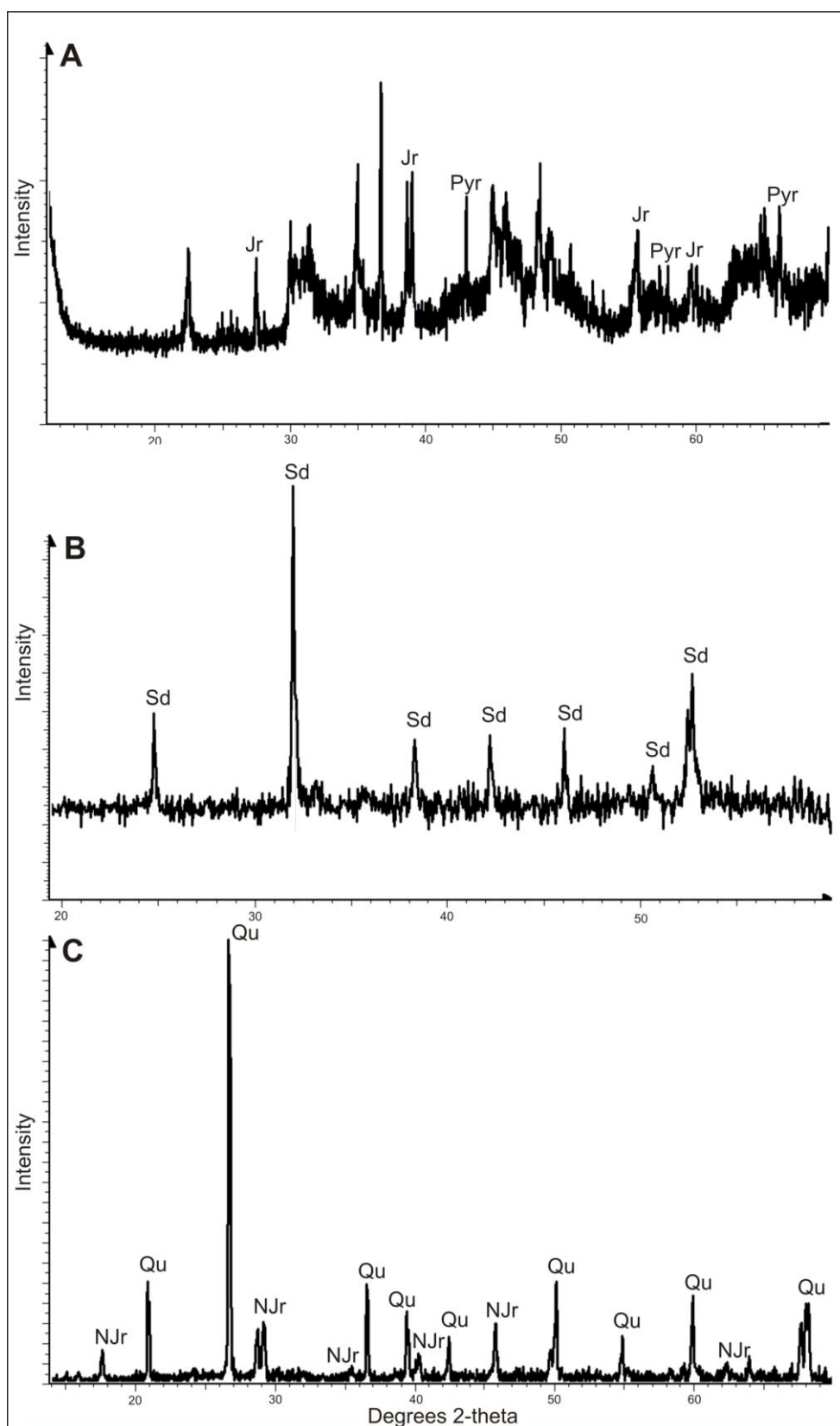


Figure 5.8 - A- typical XRD trace from Site 1 showing pyrite- Pyr, and K-jarosite- Jr peaks, **B-** ironstone XRD trace showing siderite- Sd peaks, **C-** discharge precipitate XRD trace showing natrojarosite- NJr and quartz- Qu peaks.

5.4.4 Solid chemistry

A composite surface sample of the waste at Site 1 was recovered in 2009, a year prior to the main intrusive site investigation works. ICP-MS analysis of major and trace elements was undertaken on the sample at the BGS laboratories in Keyworth, the results of selected elements from this analysis are presented in Table 5.7.

	mg/kg	wt%
Na	124	0.012
Mg	1610	0.161
Al	150667	15.067
S	9235	0.923
K	6698	0.670
Ca	243	0.024
Mn	58	0.006
Fe	78002	7.800

Table 5.7 - Selected chemical elements in composite surface sample recovered from Site 1. The analysis indicates an abundance of Fe and Al, consistent with the Fe dominant minerals, such as siderite, pyrite and goethite, and aluminiumsilicate minerals identified by QXRD analysis on similar samples from the site.

The results of the ICP-MS analysis for Fe-7.8wt% and S-0.9wt% are generally consistent with the XRD analysis of pyrite ~0.5wt% and jarosite~2wt% content in the upper 0.5m of the waste. The very low levels of Ca also support the XRD analysis which did not identify significant calcite or dolomite content in the waste.

It should be noted however that this sample was recovered from the surface of the waste which is likely to be significantly weathered causing significant reduction in the calcite, dolomite and sulphide mineral content of the waste and therefore the Fe, S and Ca content. This analysis therefore is only indicative of presence of iron and sulphate minerals and is not representative of XRD analysis of waste recovered at depth in the waste pile.

5.4.5 Sampled waters

The principal discharge stream (N) at the site was sampled on 3 occasions; prior to the site investigations works (2009), immediately following the works (2010) and once a year after the works (2011). The secondary NE discharge stream was sampled once in 2010. Two downstream samples D1 and D2 were recovered as part of the works in addition to groundwater samples recovered from BH6 and 7 installed into the peat to the south of the site. Samples of water were not recovered from boreholes installed into the waste pile (BH's 2-5) as the installations were not found to penetrate the saturated zone.

All the sampled discharge waters from the N and NE show low pH (2.2-3.47), high conductivity (740-2170 μ s/cm) and contain elevated levels of iron, Fe, and sulphate, SO_4^{2-} , up to a maximum of 158.7 and 807.03 mg l^{-1} respectively. The reduced iron species, Fe^{2+} , dominates over the oxidised species, Fe^{3+} . Speciation modelling, where $\text{Fe}^{2+}/\text{Fe}^{3+}$ was not analysed, generally indicates the dominance of Fe^{2+} , except in N-2011, and in all samples indicates the FeSO_4 species to be of secondary dominance. Mn^{2+} and MnSO_4 were modelled as the dominant manganese species. The discharge streams at the site can be classified as 'net acidic and sulphate dominant' in accordance with the scheme proposed by Younger (1995). All N and NE discharge waters are classified as Ca- SO_4 dominant waters using the Facies Piper groundwater classification convention. Downstream waters, D1 and D2, tend towards 'net acidic sulphate moderate' likely due to the formation of sulphate and iron bearing precipitates following discharge i.e. the Na-jarosite precipitates identified by XRD analysis and the observed amorphous trace stream bed ochres.

Calcium, Ca, and magnesium, Mg, in the N and NE discharge waters are considered to be elevated and are probably related to carbonate mineral dissolution and weathering facilitated by the low pH and acidity of the waters. Aluminium, Al, (up to 7.35mg/l) and manganese, Mn, (up to 19.37) concentrations are also high; this is a characteristic of low pH mine water drainage. Redox values in the discharge waters were relatively high (up to 682 mV), dissolved oxygen was only analysed once,

Location	N	N	N	NE	D1	D2	BH6	BH7
Date	23.11.2009	21.10.2010	09.08.2011	21.10.2010	21.10.2010	21.10.2010	02.11.2010	02.11.2010
Downstream	0	0	0	0	90m	1000m	n/a	n/a
Temp (°C)	10	10	19	9.5	6.6	8.4	10.4	10
Eh (mV)	681.9	-	582	-	694	757	237.5	243.1
pH	3	3.3	3.47	2.2	2.6	3	5	5
Dissolved Oxygen	10.61	-	9.1	-	-	-	-	-
Conductivity (µS/cm)	740	1268	1041	2170	1160	853	103	421
Ca	38.9	118.3	97.2	170.1	47.7	35.1	-	-
Mg	5.56	12.26	10.88	17.69	6.35	4.47	-	-
Na	10.7	11.5	9.9	10.9	11.4	7.3	-	-
K	0.7	0.58	0.53	0.56	42.13	18.5	-	-
HCO ₃ ⁻	<5	<5	<5	<5	<5	<5	-	-
Cl ⁻	15.54	12.34	12.00	11.48	42.05	18.86	-	-
SO ₄ ²⁻	268.23	490.19	569.46	807.03	217.08	157.05	5.11	2.97
NO ₃ ⁻	0.38	1.00	0.21	1.95	2.58	0.91	-	-
Fe _{tot}	27.60	129.00	127.91	158.70	28.84	16.78	2.65	1.40
Fe ²⁺	15.7	125.18	70.375	70.38	19.86	16.461	1.89	1.12
Fe ³⁺	11.9	3.93	88.325	88.33	8.98	0.319	0.77	0.28
Mn	4.58	14.23	11.90	19.37	6.01	4.37	0.07	0.02
Al	5.03	6.56	7.35	4.01	5.12	2.00	0.73	0.37
SiO ₂	23.79	35.40	40.67	33.4	26.7	13.3	n/a	n/a
Balance (%)	-4.31	11.75	3.05	4.75	5.9	1.14	n/a	n/a
WATEQ4F Speciation Model								
Phases	S.I.	S.I.	S.I.	S.I.	S.I.	S.I.		
Fe(OH) ₂ .Cl.3	5.15	4.48	5.31	3.66	4.27	3.72		
Fe(OH) ₃	-0.86	-1.5	-0.52	-2.54	-1.99	-2.32		
Goethite	4.47	3.83	5.15	2.78	3.2	3.01		
Jarosite (SS)	2.89	1.24	2.75	0.74	0.54	-0.8		
Jarosite-K	0.65	-1.02	1.32	-1.68	-2.17	-2.71		
Jarosite-Na	-2.05	-3.62	-1.16	-4.3	-4.83	-7		

Table 5.8 – Analysis from sampled discharge waters at Site1- Polkemmet Moor Ironstone. The locations correspond to the labelled locations on Figure 5.4. All analysis results are in mgL⁻¹ unless otherwise stated. n/a= not applicable, S.I. = saturation index. Where the Fe²⁺/Fe³⁺ speciation has been determined by WATEQ4F speciation modelling (as apposed to on site preservation) this is written in *italics*.

N-2009 at 10.6 mg l^{-1} which is also considered to be high, indicating the waters are not reducing in nature; this is likely due to the waste being relatively thin, up to 5m, allowing the waste to remain oxygenated. This is contradictory to the dominance of reduced Fe and Mn species and is therefore an indication of the complex redox chemistry operating at the site. This disparity could also be related to errors associated with using an equilibrium speciation model (WATEQ4F) in a scenario where redox and equilibrium conditions are rapidly changing.

Waters sampled from BH6 and 7 are more reducing ($\sim 240\text{mV}$) than that of the discharge waters. They contain some slightly elevated levels of Fe ($1.4\text{-}2.6 \text{ mg l}^{-1}$); however at much lower levels those recorded in discharge waters. This indicates that there is only limited downward movement of contaminants through the underlying peat.

Saturation indices ($\log(\text{IAP}/K_T)$) indicate all the sampled discharge waters are over-saturated with respect to goethite (FeOOH) and jarosite-ss ($\text{K}_{0.7}, \text{Na}_{0.03}, \text{H}_{0.2}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$). Consistent with the observed red amorphous precipitates and green Na-jarosite precipitates formed around the discharge streams. The downstream samples D1 and D2, which were sampled on the same day as the N (21/10/2010) discharge, show a reduction in the saturation index of goethite and jarosite species suggesting the change in water chemistry downstream is related to precipitation of these minerals. This is also consistent with XRD precipitate traces and field observations of orange ochre deposits along the length of the discharge stream, prior to confluence with the River Almond.

5.4.6 Modelling results

Figures 5.9-5.12 show the output for inverse modelling results using PHREEQC. The global uncertainty used in the inverse modelling function was set initially at 5% for each of the models, however in the models N-2010 and NE-2010 the uncertainty value was increased because the mine water discharge solution could not be balanced. In N-2010 the uncertainty value had to be increased to 16%, while in NE-2010 the uncertainty value had to be increased to 29%. This means that the inverse

solutions for these discharge water samples are likely to be less accurate in the representation of the mine water chemistry evolution than the solutions for which a 5% uncertainty value could be used, i.e. the N-2011 and N-2009 inverse solutions. This is related to the incorporation of analytical error (Percent error, $100 \cdot (\text{Cat} - |\text{An}|) / (\text{Cat} + |\text{An}|)$) in inverse calculations in PHREEQC. Most other inverse codes i.e. NETPATH do not incorporate analytical error. The incorporation of analytical error in the inverse calculations is advantageous as it increases confidence in the model results; however it means that when the water sample ionic balance is less than good, i.e. above ± 5 -10% this must be reflected in the PHREEQC inverse calculation.

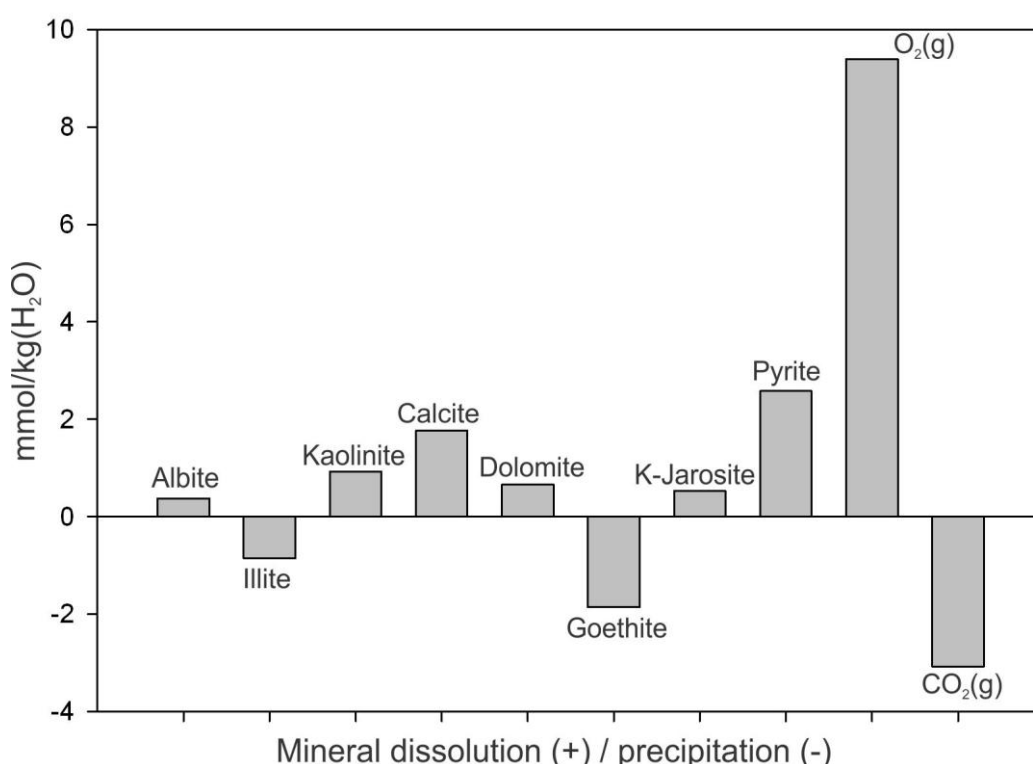


Figure 5.9 - PHREEQC inverse model results returned for the N-2011 discharge sample when using a global uncertainty of 5%. The mineralogical phases included in the model were identified by QXRD analysis. The inverse model balances the difference between rainwater entering the site and the discharge chemistry by the dissolution or precipitation of phases from the known mineralogical assemblage.

Four solutions were returned for the N-2011 inverse calculations of which one solution (Figure 5.9) included pyrite, K-jarosite and calcite, the other three solutions included only dolomite and not calcite or excluded K-jarosite in favour of K-feldspar and were therefore eliminated as possible solutions. Situations were dolomite

accounts for all the carbonate buffering at the site is theoretically valid. A prerequisite of the inverse model is that the calculations represent the evolution of water along the flow path through the entire waste pile therefore it is unlikely that dolomite dissolution occurs in isolation, particularly when considering QXRD data where calcite was identified above 1wt%. It's also considered that if present K-jarosite will be involved in the water evolution. The sum of residuals for this solution was 3.71 below the uncertainty of 5%.

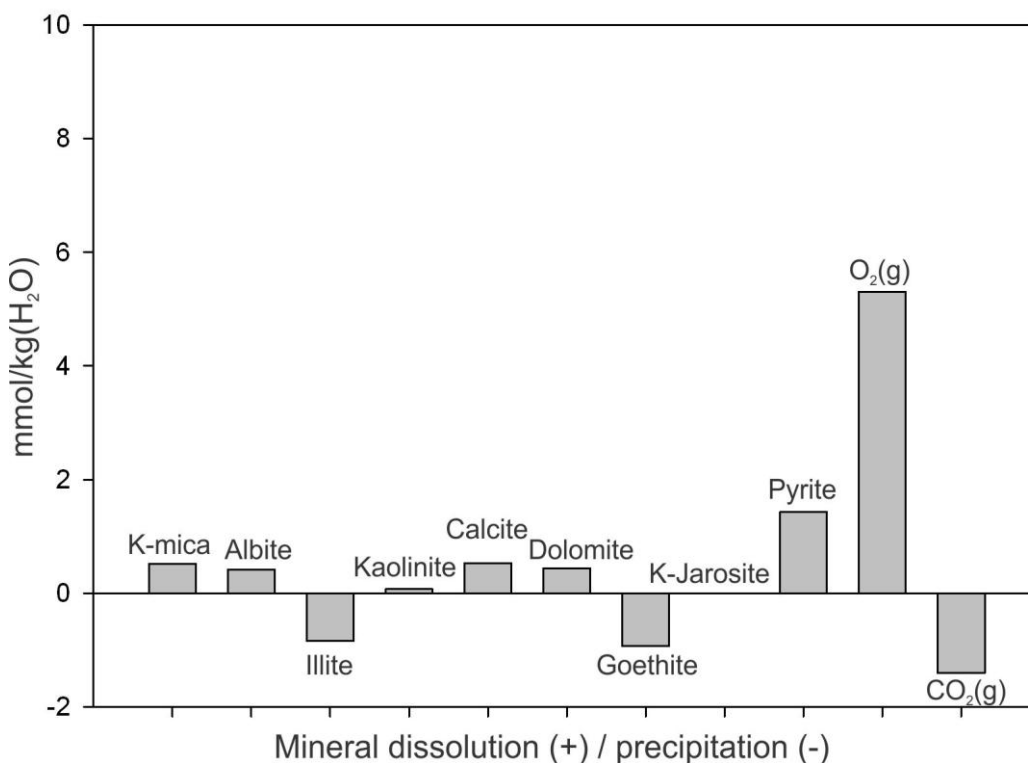


Figure 5.10 - PHREEQC inverse model results returned for the N-2009 discharge sample when using a- global uncertainty of 5%. The mineralogical phases included in the model were identified by QXRD analysis. The inverse model balances the difference between rainwater entering the site and the discharge chemistry by the dissolution or precipitation of phases from the known mineralogical assemblage.

Four solutions were returned for the N-2009 inverse calculations of which two solutions included pyrite and calcite; the other 2 solutions were eliminated. Of the two remaining solutions one was eliminated as it required dissolution of a very large quantity of siderite balanced and by a very large precipitation of goethite. Situations where siderite dissolution dominates over pyrite oxidation while at low pH are considered unfeasible. The lack of K-jarosite in this solution is an interesting feature.

The remaining solution is presented in Figure 5.10. The sum of residuals for this solution is 2.96, below the uncertainty value of 5%.

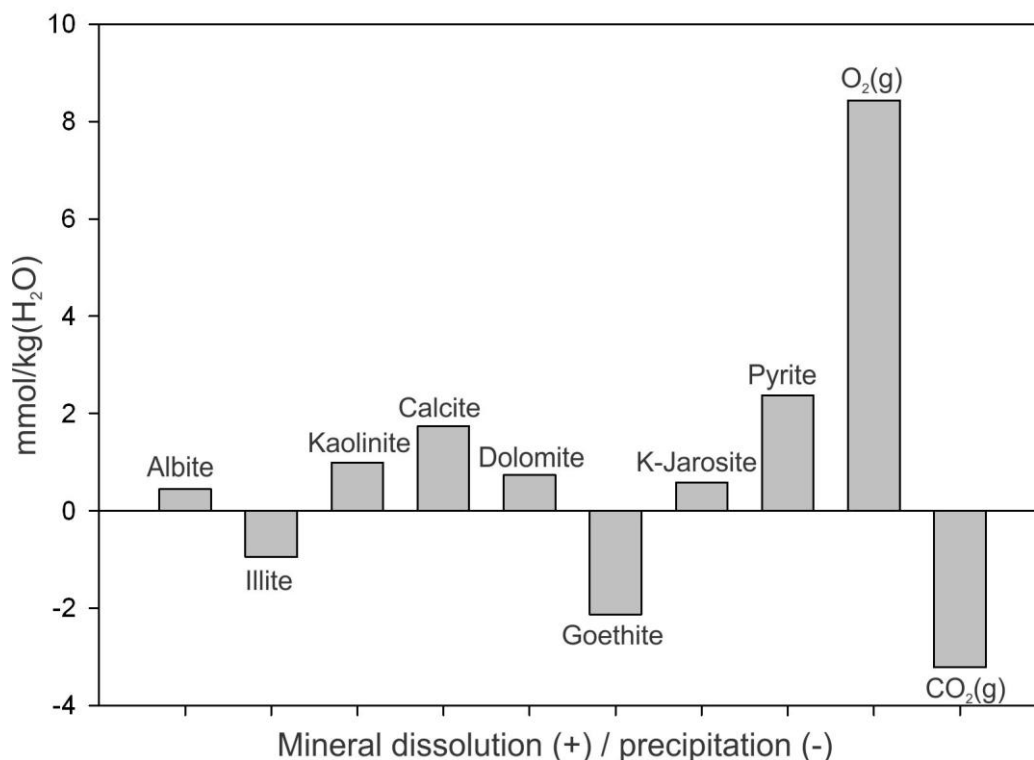


Figure 5.11 - PHREEQC inverse model results returned for the N-2010 discharge sample when using an uncertainty of 5% for rainwater, 16% for the discharge sample. The mineralogical phases included in the model were identified by QXRD analysis. The inverse model balances the difference between rainwater entering the site and the discharge chemistry by the dissolution or precipitation of phases from the known mineralogical assemblage.

Eight solutions were returned for the N-2010 inverse calculations of which two solutions included pyrite, K-jarosite and calcite. As with N-2009 of the two remaining solutions only one was considered to be feasible due to the same issue with siderite dominating over pyrite. The remaining solution is presented in Figure 5.11. The sum of residuals for this solution is 5.81, below the 16% uncertainty value used for the discharge water.

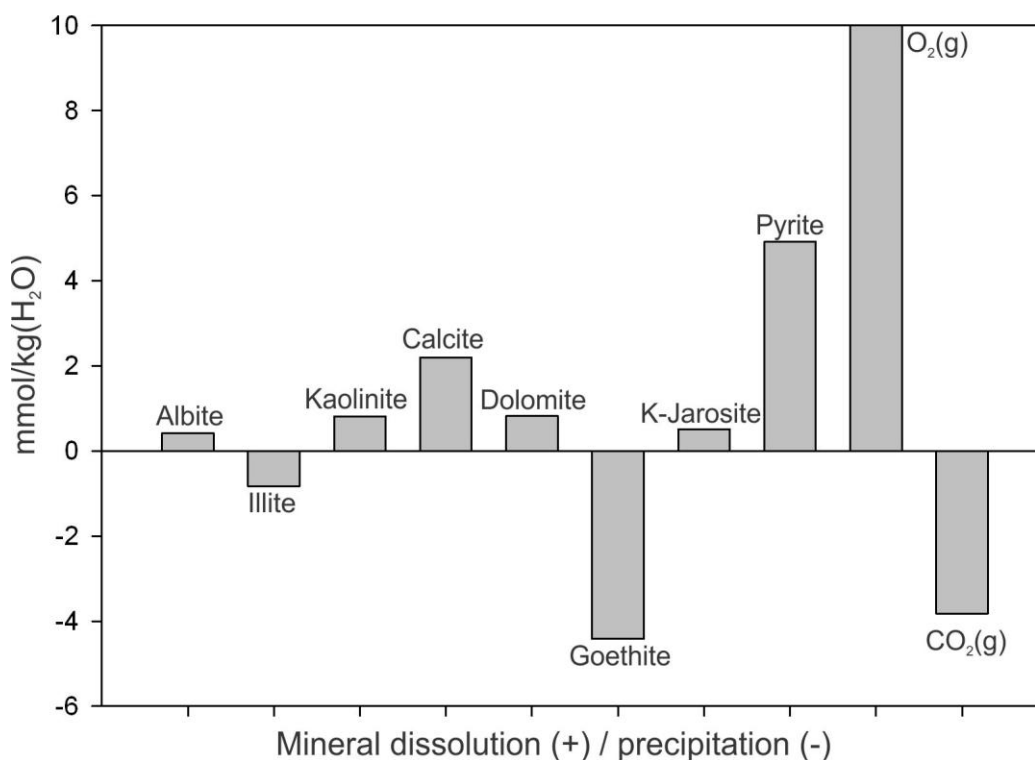


Figure 5.12 - PHREEQC inverse model results for the NE- 2010 discharge sample when using an- uncertainty of 5% for rainwater, 29% for the discharge sample. The mineralogical phases included in the model were identified by QXRD analysis. The inverse model balances the difference between rainwater entering the site and the discharge chemistry by the dissolution or precipitation of phases from the known mineralogical assemblage.

Eight solutions were returned for the N-2010 inverse calculations of which one solution included pyrite, K-jarosite and calcite. This solution is presented in Figure 5.12. The sum of residuals for this solution is 8.89, below the 29% uncertainty used for the discharge water. In isolation the high uncertainty value used in the model would probably result in the rejection of the solution however because it is similar to the other returned solution for the site it is still presented.

5.4.7 Site 1 discussion and conceptual model

Waste origin

The QXRD data for the site indicates it has a high proportion of clay or ‘argillaceous’ mineral content consistent with the observations made in the field on intrusive investigation borehole logs (Appendix B). The red orange nodules were confirmed as dominant in siderite, indicating them to be ironstone (Figure 5.8). Analytical confirmation of these observations together with the proximity of the waste to numerous mine sites and the subsurface geology at the site indicates:

- The origin of the waste to be from ironstone bands which are known to occur in the Lower and Middle Scottish coal measures (Browne et al, 1999). The Fauldhouse area is known to be one of several important areas targeted by iron companies in the late 1860s when the better quality ironstones started to become exhausted (Hassan, 1976).
- Specifically the waste is likely to be a ‘Slatyband Ironstone’ which ‘*reached its widest development as a workable subject in the ground between Fauldhouse and Harthill*’ (MacGregor et al 1923).
- Similar ironstone waste has been documented approximately 2km west of the site (Heal and Salt 1999) which was associated with the (West) Benhar colliery operated by the Summerlee Iron Company (Oglethorpe 2006).

Site hydrogeochemistry

A saturated zone is confirmed at the site by the consistent site discharges; however this was not identified in borehole installations because of their shallow nature. The use of a handheld windowless sampler, due to site access issues, resulted in boreholes only being able to be formed to ~3m bgl.. The discharge waters sampled at the site consistently showed low pH and elevated concentrations of Fe and SO₄ which is a common feature of mine waste and mines related to the oxidation of pyrite, other sulphides and hydrated sulphurous salts such as jaorsite family salts

(Wood et al. 1999; Chen et al. 1999; Younger 1995, 2000, 2001; Banwart & Malmstrom 2001; Banks & Banks, 2001, Blowes et al. 2003). QXRD data indicates that both pyrite and K-jarosite are present at significant wt% throughout the mine waste pile.

- The identified high pyrite content of the waste, up to 7wt%, is considered to be a feature of the Scottish Coal Measures Ironstone horizon from which the waste is considered to originate. This is significant because other mine waste sourced from this or similar horizons may display equally high pyrite contents.
- The K-jarosite abundance is an indicator of the ingress of oxygen into the waste as K-jarosite forms from the products of pyrite oxidation (Reaction 9, Table 5.1) (Bisson & Wills, Larsson et al 1990, Smith et al 2006) .
- The acidic and sulphate dominance of discharge waters is an indicator of the pyrite oxidation within the waste pile. This is significant as pyrite oxidation and dissolution of K-jarosite and other sulphate salts are of primary environmental concern at mine waste sites.
- The elevated concentration of Ca and Mg is another common signature in AMD environments (eg. Banwart & Malmstrom, 2001) and suggest the action of carbonate weathering which is supported by the identification of calcite and dolomite in the QXRD analysis, although their abundance is considered to be limited at close to or below 1wt%.
- Na-jarosite precipitates form in the ‘hardpan’ areas due to elevated Fe and SO₄ concentrations and low K⁺ ion concentrations. This suggest that K⁺ released in K-jarosite dissolution is recycled in the waste by the formation of further K-jarosite or is bound to abundant clay minerals.

Discharge water evolution

The use of the inverse modelling function in the PHREEQC model code offers significant insight to the dominant geochemistry operating at the site. The confidence placed in the model result is increased by the use of QXRD confirmed mineralogical phases as the model input.

All four solutions indicate rapid dissolution of the waste mineralogy:

- Pyrite oxidation (1.43-4.91mmol/kg) is the dominant source of Fe, SO_4^{2-} and acidity in the discharge waters via equations 1-4 outlined in Table 5.1.
- K-jarosite dissolution (0.51-0.59mmol/kg) is also significant in the solutions and contributes to the release of Fe and SO_4 , except in NE-2010, via equations 7 & 8 in Table 5.1.
- Goethite precipitation is effectively a sink for released Fe; equation 5 in Table 5.1
- Calcite and dolomite were present in all the model solutions, to varying degrees, indicating that the pH of discharge waters although low, at pH 2-4, is maintained at present levels by carbonate buffering via equations 11 & 13 in Table 5.1.
- Carbonate buffering does not produce bicarbonate alkalinity, as in equations 10 & 12, because of the low pH and CO_2 gas is released as shown by the negative CO_2 values in each of the model solutions.
- Aluminosilicate minerals act as acidity buffers, although to a lesser extent than carbonate buffering reactions.
- Kaolinite dissolution is the probable source for Al in discharge water, via reaction 17, and albite dissolution as the source for Na ions in discharge

waters via reaction 16. Illite is precipitated in the models probably from the combined aluminium silicate products of the other silicate dissolution reactions.

The relationship between Fe release, pyrite oxidation, K-jarosite dissolution and goethite precipitation is complex. K-jarosite for example may be precipitated at some points along the evolutionary pathway and dissolved at others. Indeed, K-jarosite would not be present in the waste pile mineralogical assemblage if it was only ever consumed as it is sourced from the products of pyrite oxidation (equation 9). The nature of the model means this complexity is not reflected in model solutions.

Pyrite oxidation mineral reactions generally involve a component of microbial catalysation, particularly at low pH values. This should also be considered when interpreting the model results because the oxygen consumption for pyrite oxidation, in reality, may be reduced, compared to the model solution, as microbes are known to facilitate the ferric iron pyrite oxidation path (equation 4, Table 5.1)

Potential environmental impact

The classification of the site discharge water as '*acidic and sulphate dominant*' and containing high Fe concentrations indicates that they have the potential for significant water quality impacts. Outlined below are the factors affecting water quality impact at the site:

- High Fe concentrations in surface waters can result in the smothering of the river bed with Fe precipitates, which cause reduced light infiltration impacting river invertebrates and the whole river eco-system (Jarvis and Younger 1997). Red orange Fe precipitates were observed along the length of the site discharge stream up to confluence with the River Almond, near Harthill. XRD analysis of these precipitates produces an amorphous trace consistent with them being iron hydroxide precipitates.
- In groundwater discharge waters could increase Fe and SO₄ concentrations which may be of concern for connected surface water bodies and abstraction

wells. The low pH of waters could also result in the mobilisation of heavy metals which are otherwise bound to aquifer materials (eg. Kjoller et al 2004).

- Mine cavities and shafts in the region, as indicated by the abundance of historic mine entries on historic maps, could potentially facilitate the movement of contaminants to groundwater. Peat offers some protection from the downward movement of contaminants in the immediate vicinity of the site.
- Downstream of the site water quality improves (samples D1 and D2) due to the precipitation of Fe and SO_4^{2-} precipitate minerals and potential from the input of non AMD impacted surface drainage waters.
- During high flow events re-suspension of precipitates has the potential to increase Fe concentrations discharged to the Almond (Chapter 4).
- Inputs of Fe from discharge water at this site are likely to make significant impact on Almond water quality: elevated Fe concentrations associated with mining is one of the principal drivers behind poor quality status river classifications in the catchment (Campbell et al. 1996, SEPA 2011).
- The low abundance of carbonate minerals in the waste suggest carbonate buffering may cease prior to acidity production in this case a drop in discharge pH and increase in heavy metal concentrations would be expected (Banwart & Malmstrom 2001). This would further increase the potential environmental impact associated with discharge waters from the site.

Conceptual models

Figure 5.13 and Table 5.9 show visual and conceptual models for Site 1 constructed based on the observations and interpretations outlined above.

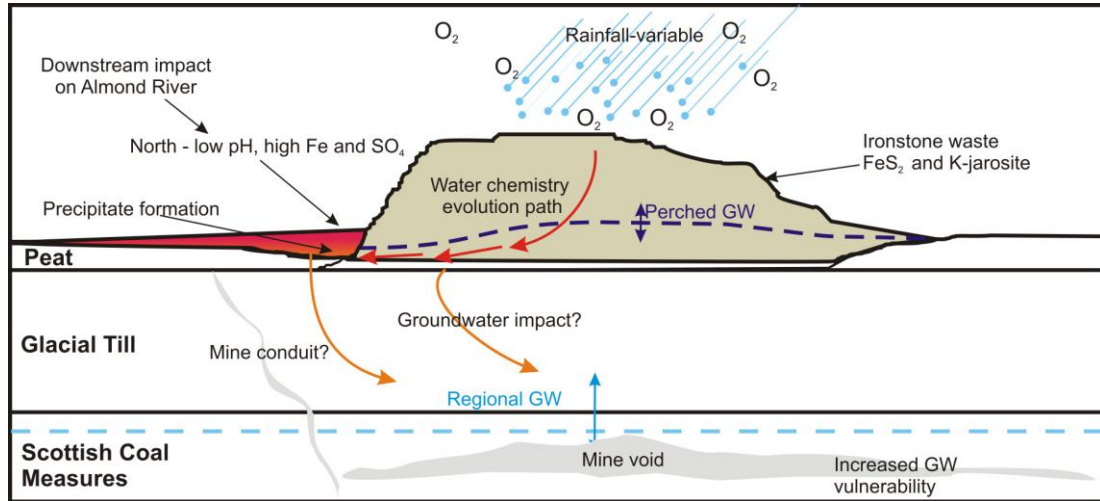


Figure 5.13 - Site 1 visual conceptual diagram indicating the principal water chemistry evolution pathway between rainfall waters and heavily mineralised discharge waters due to dissolution of the ironstone and coal measure derived mineralogy.

Table 5.9 - Site 1 –Polkemmet ironstone mine waste descriptive conceptual model

SOURCE		Identification		Description
		Identified	Identifier	
Pyrite		Yes	XRD	Up to 7wt%
Secondary AMD salts		Yes	XRD	K-Jarosite up to 4wt%
Carbonates (source buffer)		Yes	XRD	Calcite up to 1wt%, Dolomite visual identified in XRD trace <1wt% QXRD
Silicates (source buffer)		Yes	XRD	Feldspar and sheet aluminosilicates at high abundance
PATHWAY				
Discharge Chemistry	pH	2-4	Water analysis	Indication of FeS ₂ oxidation. Increases mobility of heavy metals
	Fe	Up to 159mg l ⁻¹	Water analysis	Indication of FeS ₂ oxidation. Potential issues for recipient surface water and groundwater
	Metals	Yes	Water analysis	Al, Mn and other heavy metals present. Need to consider relative impact to receptor
Human Ingestion		Possible	Site observation	Evidence of public use, particularly motorbike use. Need to consider relative impact to receptor
Superficial Geology		Peat	SI	3m thick. Reducing and higher pH compared to discharge water- may limit metal mobility.
		Glacial clays	SI	Sandy clays-generally low K. Significant potential for downward water movement due to heavily mined area.
Solid Geology		Scottish Coal Measures	BGS Maps	Moderate to high K, significant potential for mine void increasing groundwater vulnerability
RECEPTOR				
Surface Water		Yes		Fe and Fe-SO ₄ precipitates along discharge stream and probable impact on wider catchment water quality.
Groundwater		Yes		Peat groundwater shows slightly elevated Fe. Interactions between surface water and groundwater in the catchment are likely to occur. Possible direction contamination to regional groundwater beneath the site. Peat may limit impacts, mine shafts and cavity may increase impacts
Human Health		Possible		General deterioration of water environment. Possible dust inhalation during summer months from site users.

5.5 Site 2- Whitrigg colliery mine waste

Site 2 is located in East Whitburn at NS 9670 6457, approximately 1.2km east of the town centre of Whitburn in West Lothian. It can be accessed from a small road off the A705 which provides access to industrial units now located in the centre of the site as well as the vegetated public area formed as part of the site redevelopment.

5.5.1 Site history

Whitrigg colliery (Pit No. 5) and associated mine waste pile first appears on the 2nd revision Lanarkshire Sheet county series 1:2500 OS map survey in 1914 (Figure 5.16), however, the colliery was operational from 1900 to 1972 (Oglethorpe, 2006). The colliery targeted deep coals (No5 Shaft- 323m) in the Upper Limestone Formation, Limestone Coal Formation and potentially the Lower Limestone Formation which are stratigraphically below the Passage group. Surface waste deposits which remain at the site today are likely to have been accumulated from several lithological horizons as the mine progressed. This was observed on historic maps by the gradual increase in the volume of mine waste around shaft No5 over the lifetime of the mine. It appears from the historic plans that the main shaft at the former mine site is covered by part of the central area of the waste pile. Several settlement ponds, contained within the waste are noted on historic maps. Settlement ponds were often used as a mine phase remediation measure to prevent the washing of ‘coal solids’ downstream (Brock 1982).

In the early 2000s the site was landscaped, capped and vegetated and a mine water treatment system was constructed with the aim to reduce impact on the local ‘Latchburn’ water course (Entec 2004).

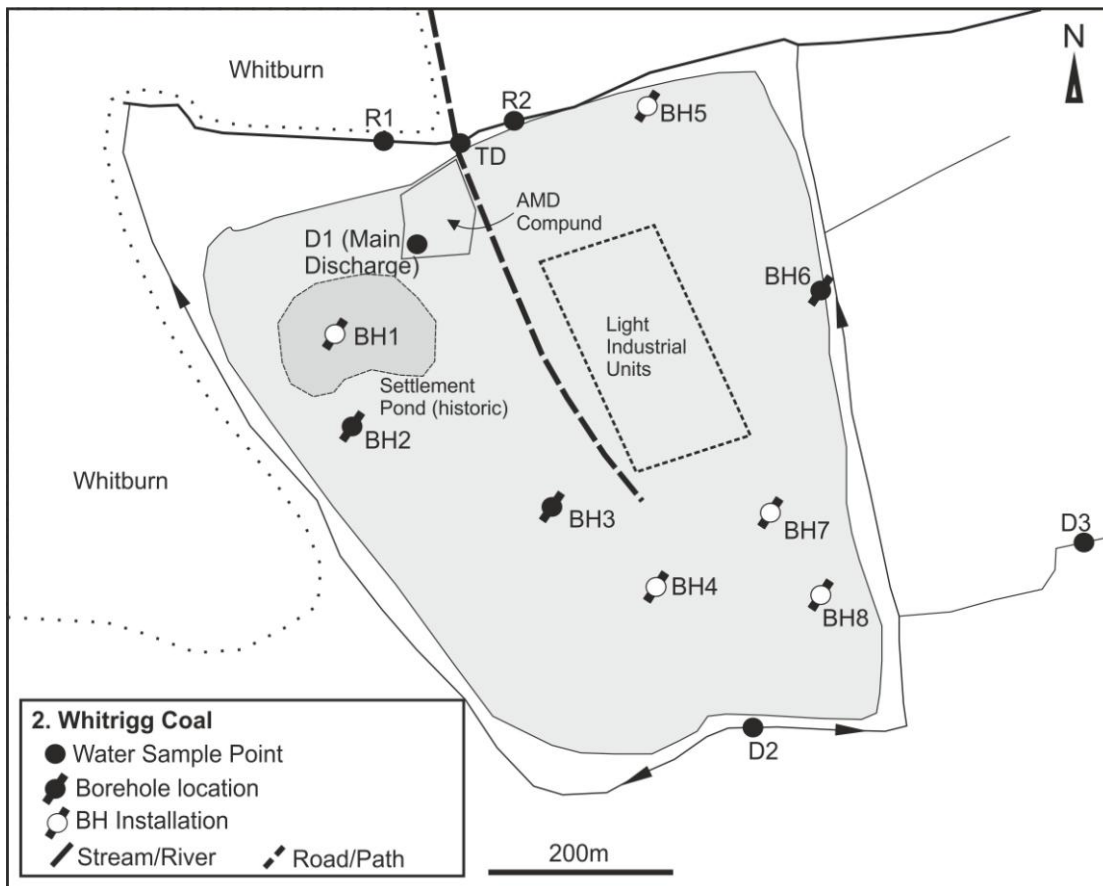


Figure 5.14 - Site 2 site investigation works plan showing the waste pile (grey) and eight boreholes drilled into the waste as part of the works. Water and discharge sample positions on the surface drainage trenches around the site and at the main site treatment area are also shown (black circles). The central area of the site containing the path and light industrial units is low in elevation, the area of highest elevation is to the south (around BH4).

5.5.2 Ground conditions

Site overview

The site consists of approximately 550,000m² of dark grey mudstone and fine sandstone mine waste with one principal mine water discharge stream to the north which is treated by the passive treatment system before being discharged to the Latchburn, which then discharges into the River Almond approximately 1.1km downstream, close to the town of Blackburn. The treatment system, which significantly reduces the Fe concentrations, discharges into Latchburn at a flow rate of between 0.5-1 ls⁻¹ (Heal et al, 2006) however extensive stream bed ochre deposits are still observed in the Latchburn (Figure 5.15). A drainage channel encompasses the site to collect other less significant mine water discharges and surface run off,

this partially drains to the east in a small stream close to Moss Hall farm where more stream bed ochre deposits are observed.

The mine waste itself in the central area is up to 25m in height when compared to the agricultural fields to the south and east. As part of its redevelopment, for public recreational use, the mine waste has been graded with a shallow angle towards the north, at the entrance to the site, and a steeper angle on its southern edge. It has also been capped with a layer of clay and soil and heavily vegetated with predominantly evergreen trees. The general topography of the surrounding area dips towards the north hence the main discharge site discharge being found to the north.



Figure 5.15 - Photograph of Latchburn streambed Fe precipitates close to the main discharge point from the site. The orange coloration of the streambed is due to the oxidation and subsequent precipitation of Fe discharged in site waters. This results in ecological impacts to the river's bio-diversity.

Intrusive site works

Site investigation at the site involved sampling and borehole installation formed using a tracked Dando window sample rig. Eight intrusive boreholes were formed,

all with the waste itself, five of which (BH 1, 4, 5, 7 & 8) were installed with small diameter piezometers. No boreholes were drilled in the surrounding areas.

Boreholes in the waste were formed to a maximum depth of 5mbgl, mine waste samples were recovered every 0.25-0.5m. The recovered waste although layered and locally variable is described as a light to dark grey sandy gravel of mudstone and fine grained sandstone with occasional black coal fragments. Some of the surfaces of gravels show evidence of sulphide mineral oxidation due to orange and yellow mineral precipitate formation. This is an indication of water and oxygen moving through the waste, however it should be considered that this oxidation maybe a relic of the mine waste pile prior to redevelopment. In BH1 a layer of extremely wet black silty sand was encountered between 1 and 5mbgl with a groundwater strike at approximately 3mbgl (Borehole logs are available in Appendix B). Consultation of historic maps revealed this area to be the site of a large historic settlement pond (Figure 5.16). This suggests the pond sediments were left in situ and covered with a thin layer of waste and clay during the redevelopment. No other significant groundwater strikes were encountered in any of the other boreholes during formation and the waste was generally dry.

BH5 showed a red to brown, occasionally pink to white, sandstone and mudstone dominant lithology. It's possible that this area of the redeveloped waste pile may have incorporated mine waste from the 'Whittrigg Fireclay Mine' which occupied the land to the north east of the main site (Figure 5.16). At 4.7mbgl in BH5 the waste material became distinctly wet, although no definite groundwater strike was noted.

The BGS 1:50,000 geological maps for the area indicate the site is underlain by Devensian till deposits; however it's likely these have been significantly broken or removed in the central area of the site to facilitate the formation of mine shafts at the colliery. The solid geology below the site on BGS maps is shown to be at the contact between the Passage Group sandstones to the west and the Upper Limestone Formation to the east.

Groundwater

Borehole	GW Strike (mbgl)	Base (mbgl)
BH1	4.0	5.0
BH4	4.8	5.0
BH5	3.5	5.0
BH7	No GW strike	5.0
BH8	No GW strike	5.0

Table 5.10 - Groundwater level monitoring from borehole installations at Site 2 on the 24/11/2010. Borehole positions are shown on Figure 5.14

Borehole installations in the mine waste pile at Site 2 were monitored on 24/11/2010. Groundwater was encountered at between 3.5 and 4.8 mbgl in BH 1, 4 & 5. No groundwater strike was recorded in BH 7&8. This indicates a significant thickness of perched groundwater aquifer in north and central areas of the waste pile as the pile is up to a maximum of 25m in height. Groundwater is also likely to be present in the rest of the waste pile but below the monitoring depth of 5m in BH7 and BH8.



Figure 5.16 - Site 2- Whitrigg Colliery 1957 National Grid 1:2500 –(Landmark Information Group). Whitrigg Colliery (No.5) showing historic mine head buildings and mineral railways, mine waste arrangement (prior to redevelopment), large settlement ponds and associated fireclay mine to the north east.

5.5.3 Mineralogy

The results of QXRD analysis on the 23 samples recovered from BH 1, 2 and 7 at variable depths up to 4.8m are presented in Table 5.11. Analyses indicate that the waste consists predominantly of clay and sheet silicate minerals with minor fractions of quartz, feldspars and carbonates.

Phase	Formula	n	Max	Median	Min
Quartz	SiO ₂	23	2.2	1.4	0.9
Microcline	KAlSi ₃ O ₈	23	7.3	3.1	0.7
Albite	NaAlSi ₃ O ₈	1	1.1	1.1	1.1
Orthoclase	KAlSi ₃ O ₈	21	4.9	2.3	0.0
Dickite	Al ₂ Si ₂ O ₅ (OH) ₄				
Illite	K _{1.5-1.0} Al ₄ [Si _{6.5-7.0} Al _{1.5-1.0} O ₂₀](OH) ₄	23	55.2	40.0	12.3
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	23	52.2	22.6	11.7
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	23	36.4	22.4	17.0
Calcite	CaCO ₃	23	3.9	0.2	0.0
Dolomite	(CaMg)(CO ₃) ₂	23	1.0	0.3	0.0
Siderite	FeCO ₃	1	2.2	2.2	2.2
Pyrite	FeS ₂	23	1.5	0.1	0.0
Jarosite	KFe ₃ (SO ₄) ₂ (OH) ₆	23	1.7	0.2	0.0
Goethite	FeOOH	23	1.2	0.6	0.1
Hematite	FeO ₂	1	1.3	1.3	1.3

Table 5.11 - QXRD mineralogical analysis results (in wt %) returned by the reitveld analysis from 23 samples recovered at various depths from boreholes drilled at Site 2.

Iron and Sulphate Minerals

Pyrite and K-jarosite XRD peaks were identified in a number of traces, however their abundance in the majority of the 23 samples analysed fell below the effective QXRD detection limit of 1wt%. Pyrite exceed 1wt% in BH7 at 2-3 mbgl and was recorded at 0.92wt% in BH1 at 4.4mbgl. K-jarosite was analysed at 1.7wt% in BH1 at 2.8mbgl. BH1 between 1 and 5mbgl penetrates the historic settlement pond sediments at the site; a comparison between the XRD traces at three depths in the horizon is presented in Figure 5.17. The K-jarosite diagnostic peaks, at ~38° and ~50°, are clearly evident in the trace returned for 2.8mbgl while the diagnostic pyrite peak, at ~36°, is most evident in the 4.4mbgl trace; the peaks in 4.8mbgl are less obvious though there is a slight indication that both pyrite and jarosite may be present in the sample.

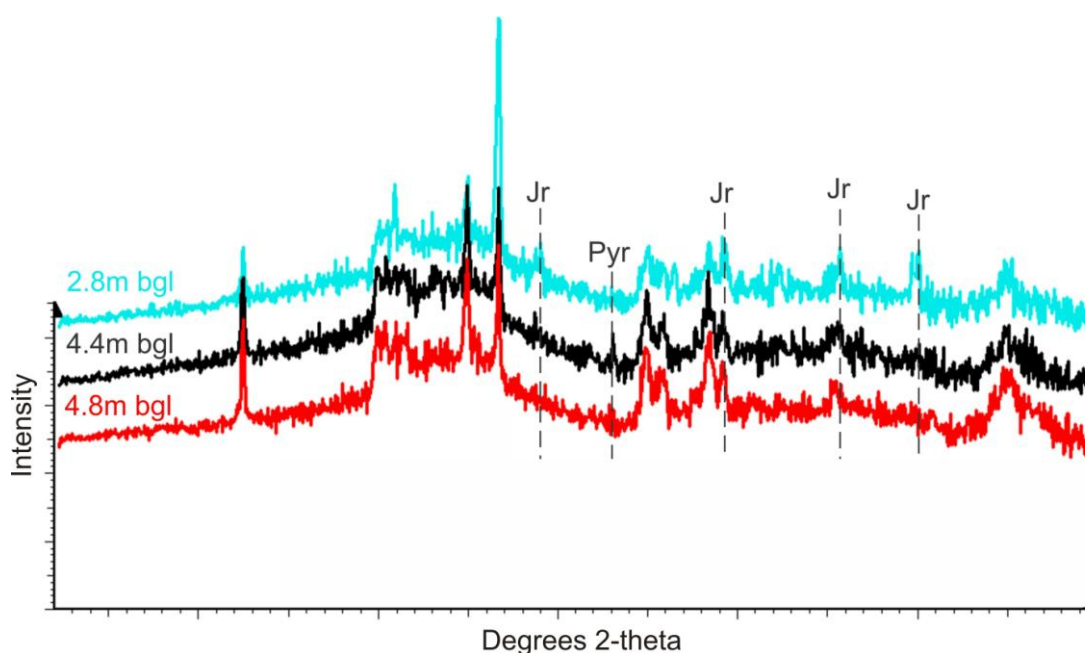


Figure 5.17 - XRD traces from settlement pond sediment horizons in BH1- with highlighted diagnostic K-jarosite (Jr) and pyrite (Pyr) peaks. The depth of the samples from each traces in indicated on the left. The best indication of significant pyrite content is in the sample at 4.4m bgl, while the best indication of jarosite is in the sample at 2.8m bgl.

As with Site 1, pyrite and K-jarosite are the main iron and sulphur bearing minerals detected at the site and although the pyrite content of the rest of the waste is low it's likely other unidentified 'hotspot' areas like those identified in BH1 and BH7 exist throughout the waste pile. .

Carbonates and silicates

Calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) are recorded at low levels, generally below 1wt%. In BH1 at 0.8 and 1.4mbgl calcite was analysed at 2.28 and 3.9wt% respectively. Dolomite was not recorded above 1wt% in any of the analysed samples. As with the waste at Site 1 this is significant because it means that the potential carbonate buffering capacity of the waste is limited. This site, however, is complicated by the installation of the anoxic limestone trench as part of the treatment system.

Microcline and Orthoclase were identified in the majority of the analysed samples with median values of 3.1 and 2.3 wt% respectively. Kaolinite and muscovite were

identified as major constituents of the waste mineralogy with approximate median values of 20wt%.

5.5.4 Sampled waters

The principal discharge D1 at Site 2 was sampled following the intrusive site investigation work on the 15/11/2010; the drainage channel which runs around the site D2 was also sampled as well as two boreholes (BH 1&4) and two samples from latch burn, before, R1, and after, R2, the discharge from the treatment compound. In previous mine water investigations a sample associated with the site was recovered from a drainage channel running eastwards towards Mosshall farm-D3. D1 was sampled before the reed beds and settlement lagoons of the passive treatment system; discharge water at this point has already passed through the buried anoxic limestone trench.

The main discharge shows high conductivity (1697mS/cm), iron (Fe -78.6mgL⁻¹) and sulphate (669.06 mgL⁻¹) with a slightly acidic pH - 6.2. The reduced iron species, Fe^{2+} , dominates over the oxidised species, Fe^{3+} . Speciation modelling indicates that FeSO_4 and FeHCO_3^+ are significant. The main discharge water is classified using the Younger (1995) scheme as 'alkaline and sulphate dominant' and as Ca-SO_4 dominant using the Facies Piper groundwater classification convention. The redox potential of the principal discharge (227.8mV) although not low compared to some mine waters is considered to be reduced, this is likely related to the waste being of considerable thickness, ~25m, restricting the infiltration of oxygen into the lower region of the waste pile. The clay cap on the waste is also likely to further restrict in the infiltration of oxygen and impact water chemistry (Gandy & Younger 2003).

The main discharge water contains elevated levels of Ca (217mgL⁻¹), Mg (52.4mgL⁻¹) and bicarbonate, HCO_3^- (188mgL⁻¹) indicative of mine waters which have been significantly buffered by carbonate mineral reactions (Banwart & Malmstrom 2001, Wood et al 1999). This is likely to be related to the limestone trench through which the waters pass as well as any natural buffering capacity of the waste mineralogy.

Location	D1	D2	D3	R1	R2	BH1	BH4	TD
Description	Main Discharge	Rear drainage	Mosshall Farm	Latchburn-Pre discharge	Latchburn- Post discharge			Treatment Discharge
Date	15/11/2010	15/11/2010	05/11/2009	15/11/2010	15/11/2010	24/11/2010	24/11/2010	05/11/2009
Temp (°C)	8.9	6.2	9.1	7.2	6.7	8.2	8	7.6
Eh (mV)	227.8	363.5	344			316	-	678.1
pH	6.2	6.1	7.5	6	6.1	5.5	5.8	3.7
Conductivity (µS/cm)	1697	219	373	344	586	929	2700	1288
Ca	217.3	24.3	35.2	35.5	67.9			148.8
Mg	52.43	5.6	9.03	7.4	16.34			49.8
Na	6.9	5.3	5.2	10.4	11.2			7.6
K	10.65	2.43	40.9	2.06	9.91			32.2
HCO ₃ ⁻	188	61	121	90	95			<5
Cl ⁻	6.01	6.69	45.12	10.86	14.75			31.24
SO ₄ ²⁻	669.06	22.59	15.70	39.95	127.90	159	314	640.36
NO ₃ ⁻	1.35	2.30	0.77	5.13	4.40			3.897
Fe _{tot}	78.60	0.31	0.80	0.79	1.31	6.66	0.001	0.7
Fe ²⁺	67.30	0.76	n/a	0.79	1.30	7.12	n/a	n/a
Fe ³⁺	11.3	n/a	n/a	n/a	0.099	n/a	0.001	n/a
Mn	12.10	0.19	0.80	0.48	1.87	3.75	3.24	8.50
Al	0.061	0.165	0.030	0.050	0.041	0.029	0.005	2.600
SiO ₂	33.46	11	12.1	13.1	14.2			26.8
Balance	5.59	8.54	0.9	4.37	8.68			-4.6
WATEQ4F Speciation Model								
Phases	SI	SI						
Fe(OH) ₂ .Cl.3	8.82	-						
Fe(OH) ₃	3.9	-						
Goethite	9.18	-						
Jarosite (SS)	8.37	-						
Jarosite-K	6.95	-						
Jarosite-Na	2.86	-						
Siderite	0.56	-1.65						

Table 5.12 - Sampled waters from Site2- Whitrigg Colliery- the location of each sample corresponds to the location on Figure 5.14. Units are all in mgL⁻¹ unless otherwise stated. n/a= not applicable, S.I. = saturation index. Where the Fe²⁺/Fe³⁺ speciation has been determined by WATEQ4F speciation modelling (as apposed to on site preservation) this is written in *italics*.

Saturation indices ($\log(\text{IAP}/K_T)$) produced by speciation modelling undertaken in PHREEQC using the WATEQ4F database indicate the water is significantly over-saturated with respect to iron oxyhydroxides ($\text{Fe}(\text{OH})_3$), goethite and selected jarosite group minerals. Water sampled from BH1 which penetrates the top of the settlement pond sediments also contains elevated Fe (6.6mg l^{-1}) and SO_4^{2-} (159 mg l^{-1}).

Latchburn although receiving water from the main discharge following treatment shows evidence of influence from the treated discharge; Fe and SO_4^{2-} concentrations are increased from 0.79 to 1.31 mg l^{-1} and 39.9 to 127.9 mg l^{-1} respectively (between R1 and R2). The stream bed is also covered in orange red iron precipitates.

Water recovered from the drainage channel at the rear of the site, D2, shows a different chemistry to that of the principal discharge. It has much lower concentrations of all the major ions and Fe concentrations of 0.7mg/l . D3, while containing Fe at 0.8mg/l , shows a water type with low SO_4 concentrations which is considered to have significantly altered chemistry compared to its potential source at the site.

The TD sample recovered in 2009 indicates that the treatment system effectively removes a considerable percentage of the Fe in discharge waters reducing Fe to 0.7mg l^{-1} . However the waters still contain elevated concentrations of SO_4 and a much lower pH at 3.7 than the D1 discharge.

5.5.5 Modelling results

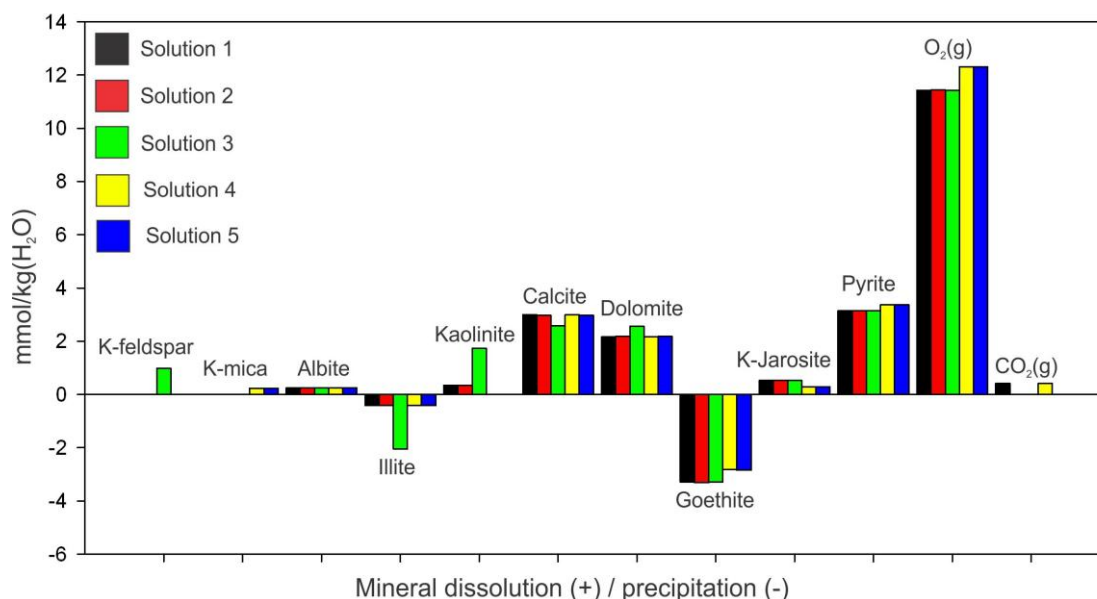


Figure 5.18 - PHREEQC inverse model results returned for the D1 discharge sample at Site 2 when using a global uncertainty of 5%. The mineralogical phases included in the model were identified by QXRD analysis. The inverse model balances the difference between rainwater entering the site and the discharge chemistry by the dissolution or precipitation of phases from the known mineralogical assemblage.

Twelve solutions were returned for the D1 inverse calculations of which five solutions (Figure 5.18) included pyrite, K-jarosite and calcite, the other seven were excluded principally as they did not include K-jarosite which is considered to be involved in the water evolution due to its identification in the ‘settlement lagoon’ horizons of BH1. The sum of residuals for solutions 1,3 and 4 is 6.26, and for solutions 2 and 5 is 8.09.

5.5.6 Site discussion and conceptual model

Waste origin

The location of the site together with historic evidence and QXRD mineralogy analysis indicates:

- The waste originated from the Upper Limestone Formation and possibly partially from the Passage Group sandstones beneath the site. The waste site is sizeable and as such is likely to contain waste from a variety of mined horizons, particularly as the colliery was deep (Pit No.5, 323m deep, Oglethorpe 2006).
- No carbonate dominant rock types suggesting limestone and other carbonate rich rocks were largely undisturbed in the mine.
- The waste in the north east of the site (BH5) differs from the rest of the site suggesting it may have originated elsewhere, possibly from the ‘Whitburn Fireclay Mine’.

Site hydrogeochemistry

- Monitoring of water levels in installations indicates a significant saturated thickness in the mine waste pile.
- QXRD analysis indicates specific pyrite and K-jarosite ‘hotspots’ in the waste which are considered to be of principal control on the evolution of the sampled discharge waters. Most significant is the settlement pond ‘hotspot’ located in close proximity to the main discharge stream.
- The bulk of the waste (not associated with the settlement pond) although only containing pyrite and K-jarosite above 1wt% in one identified ‘hotspot’ area in BH7 may also contribute to the discharge evolution. Either from other

‘hotspot’ areas not identified in the site works or from oxidation and dissolution reactions (Table 5.1) in waste with less than 1wt% pyrite and K-jarosite.

- The waste is generally lacking in carbonate content. The pH of waters in boreholes is less than those recorded in the main discharge stream indicating the influence of the anoxic limestone trench.

Discharge water evolution

Consideration of the limitations of the PHREEQC inverse function, outlined previously, should be borne in mind when interpreting the inverse solutions. Model solutions indicate rapid dissolution of the waste mineralogy accounts for the sampled water chemistry:

- Pyrite oxidation (3.12-3.37mmol/kg) and K-jarosite dissolution (0.29-0.54mmol/kg) are the dominant source for Fe, SO_4^{2-} recorded in the discharge chemistry.
- Precipitation of goethite (2.82-3.34mmol/kg) acts as a partial sink for released Fe.
- Pyrite oxidation is facilitated by the consumption of oxygen (11.37-12.3mmol/kg) and where pyrite oxidation is increased in a model solution a corresponding increase in oxygen consumption is observed. This indicates the importance of the availability of oxygen to pyrite oxidation and contaminant production at the site, particularly significant as the site has been capped to try to reduce oxygen infiltration. As with Site 1 the solutions do not allow for potential K-jarosite precipitation associated with pyrite dissolution along the water evolutionary path as net input/output mass balance models.
- Carbonate mineral reactions are dominant in the model solutions (calcite (2.58-2.99mmol/kg) dolomite (2.16-2.57mmol/kg)), maintaining the pH at 6.2 by buffering of acidity.

- Aluminosilicate minerals also buffer acidity. In solutions 1 and 2 albite (0.26mmol/kg) and kaolinite (0.37mmol/kg) dissolution consume acidity while releasing Na and Al. Illite is precipitated (-0.44mmol/kg) from the aluminium silicate products of silicate mineral reactions together with K^+ likely released from the K-jarosite dissolution. In solution 3, K-feldspar dissolution (0.98mmol/kg) results in the increased release of K^+ which facilitates increased kaolinite dissolution (1.76mmol/kg) and illite precipitation (2.07mmol/kg). In solutions 4 and 5 the dissolution of K-mica (0.25mmol/kg) and the increased oxidation of pyrite (3.37mmol/kg) limit K-jarosite dissolution (0.29mmol/kg). Between solutions 1 and 2 and 4 and 5 the consumption of O_2 and CO_2 results in small changes in the dissolution of calcite and dolomite accounting for the generation of bicarbonate, HCO_3^- , alkalinity.
- In reality, a combination of each of the 5 solution scenarios are likely to occur along the water evolutionary pathway, dependent upon the availability of carbonate and silicate minerals, O_2 and CO_2 .

Potential environmental impact

The classification of the discharge water at the site as '*(slightly) acidic and sulphate dominant*' indicates that they have the potential to impact the surface water environment but less so than other more acidic mine water discharges (Younger 1995). The passive treatment system at the site significantly reduces the loading of mine related contaminants which are discharged into surface waters (Latchburn) and is designed to increase alkalinity of waters. In Heal et al (2006) the summer time, low flow, mass removal of acidity and soluble Fe was calculated between 80-95%. This is consistent with the difference in Fe concentrations in D1 and TD sampled waters. However, the samples recovered from Latchburn indicate that the discharge, even following treatment, increases Fe concentrations in the stream, also noted by Heal et al (2006), and results in the formation of Fe stream bed precipitates (Figure 5.15). The treatment system could be considered to be under performing as, while

waters at D1 are buffered to pH-6.2, in TD the pH was recorded at 3.7. This is probably related to iron precipitation in the treatment system releasing proton acidity, H^+ , via reaction 4 shown in Table 5.1.

- The release of low pH waters is of concern due to increased heavy metal mobility in the water environment while the observed Fe precipitates will have a direct impact on the water quality in Latchburn through reduced light infiltration impacting river invertebrates and the whole stream ecology (Jarvis and Younger 1997).
- Elevated Fe is a major concern in surface waters throughout the Almond River catchment (Campbell et al 1996, Pollard 2001, SEPA 2011) and the released Fe here is likely to be a contributor.
- Fe rich surface water could impact groundwater quality, both directly from surface water-groundwater interactions through the hyporheic zone in the Latchburn and diffusely from the movement of Fe in the catchment river system (Chapter 4).
- Increased flow in the Latchburn may lead to re-suspension of the observed Fe precipitates causing movement of Fe and increased water quality impacts associated with the site further downstream.
- Groundwater may also be directly impacted from perched groundwater in the mine waste moving into the regional groundwater body, possibly down former shaft No.5, below the site, or in other man made mine conduits.

Conceptual Models

Figure 5.19 and Table 5.9 show visual and descriptive conceptual models for Site 2 constructed based on the observations and interpretations outlined above.

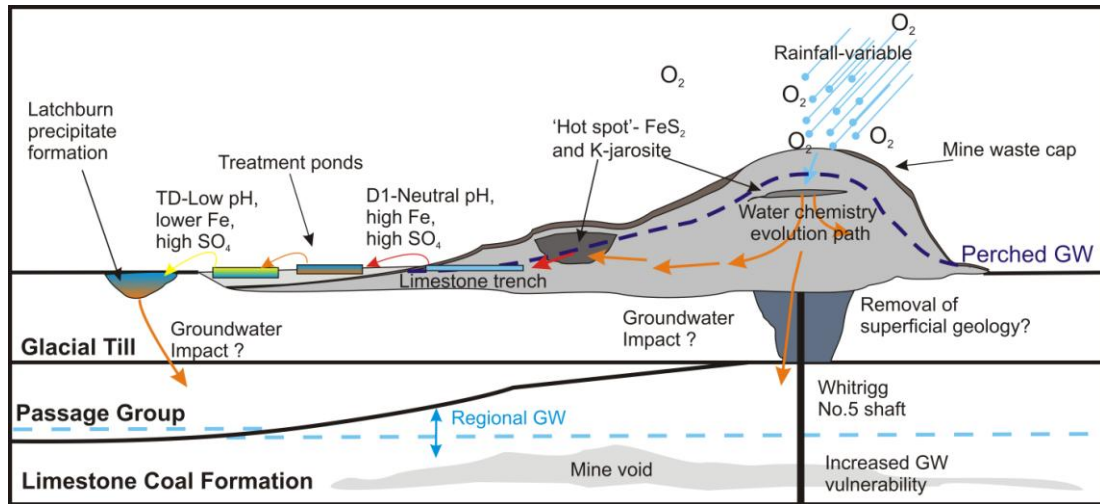


Figure 5.19 - Site 2 visual conceptual diagram indicating the principal water chemistry evolution pathway between rainfall waters and heavily mineralised discharge waters. Also shown to the left is the treatment system arrangement and 'hotspots' of higher acidic mineral content with the waste pile.

Table 5.13- Site 2- Descriptive conceptual model

SOURCE		Identification		Description
		Identified	Identifier	
Pyrite		Yes	XRD	Up to 2wt% in a limited number of samples
Secondary AMD salts		Yes	XRD	Jarosite up to 1.5wt% in a limited number of samples
Carbonates (source buffer)		Yes	XRD	Calcite up to 4wt%, Dolomite visual identified in XRD trace <1wt% QXRD, in a limited number of samples
Silicates (source buffer)		Yes	XRD	Feldspar and sheet aluminosilicates at high abundance
PATHWAY				
Discharge Chemistry	pH	6	Water analysis	Affected by site treatment. Lower at 5.5 in site BH's.
	Fe	78.6 mg l ⁻¹	Water analysis	Indication of FeS ₂ oxidation. Above 1mg l ⁻¹ post treatment. Potential issues for recipient surface water and groundwaters
	Metals	Yes	Water analysis	Al, Mn and other heavy metals present. Need to consider relative impact to receptor
Human Ingestion		Possible-limited	Site observation	Site redevelopment involved capping of the waste. Some areas in the central area of the site show exposed mine waste
Superficial Geology		Glacial clays	BGS Maps	Clays-generally low K. Significant potential for downward water movement due to former shaft below the site.
Solid Geology		Passage Group and Limestone Coal Formation	BGS Maps	Moderate to high K, significant potential for mine void increasing groundwater vulnerability
RECEPTOR				
Surface Water		Yes		Fe precipitates identified along Latchburn. Significant Fe reduction compared to main discharge chemistry but still impacts on local surface water and possible impacts on wider catchment water quality.
Groundwater		Yes		Interactions between surface water and groundwater in the catchment are likely to occur. Probable direction contamination to regional groundwater beneath the site due to historic shaft- high groundwater vulnerability due to mine void and shafts.
Human Health		Possible		General deterioration of WQ

5.6 Site 3- East Benhar mine waste

Site 3 is located on Fauldhouse Moor at NS 9162 6202, approximately 2.0km NNW of the town of Fauldhouse in West Lothian. It is accessed immediately to the west of Harthill Road between Fauldhouse and Harthill at the site of the now abandoned settlement of East Benhar. Polkemmet Colliery (abandoned) is located to the north east as is the town of Whitburn; to the south west is the town of Shotts. Site 3 is 0.5km due south of Site 1

5.6.1 Site history

The East Benhar minewaste was formed from two discrete periods of mining; the western half of the waste first appears on the 1st Revision Lanarkshire Sheet county series 1:2500 OS map surveyed in 1896. The mineral railways suggest the waste originated from the 'Fallahill Colliery'. The second half of the waste, which forms the principal conical structure, appears on the 1957 map and is associated with the 'East Benhar (Coal) Mine' (Figure 5.20). The two different mines resulted in two different mine waste rock types, the first a dark 'argillaceous' mudstone and the second being a pale yellow to grey 'arenaceous' sandstone.

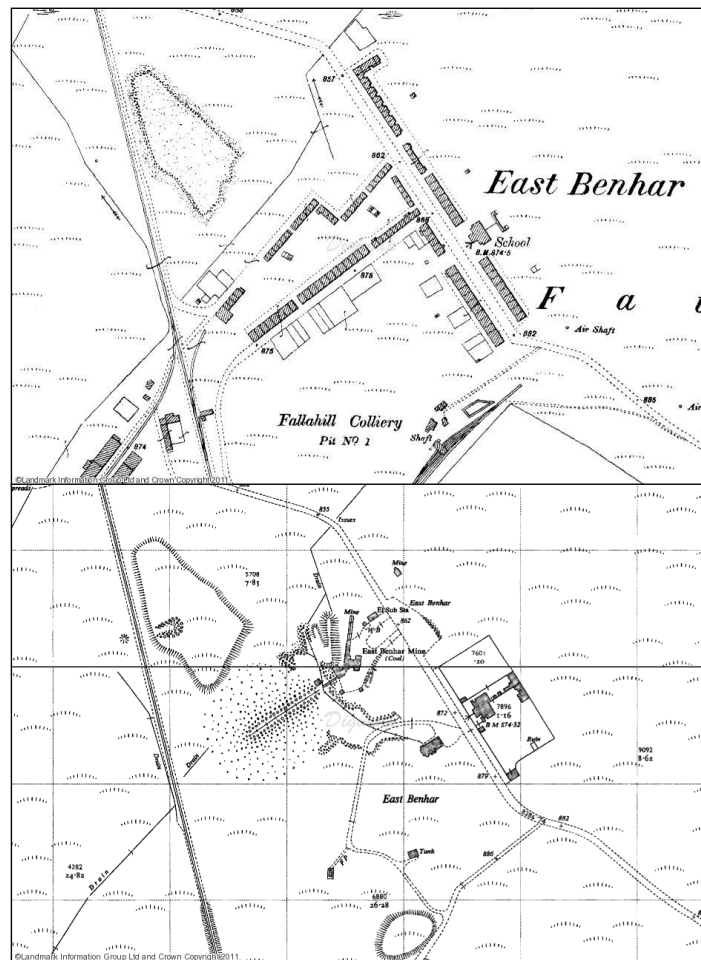


Figure 5.20 - Historic maps of benhar colliery waste- (top) 1st Revision Lanarkshire Sheet county series 1:2500 OS map surveyed in 1896 showing mine waste associated with Fallahill Colliery, (bottom) 1957 1:2500 National Grid Map showing mine waste associated with East Benhar (Coal) Mine, (Both maps reproduced from Edina Digimap, top sourced from the Landmark Information group, bottom sourced from the National Library of Scotland)

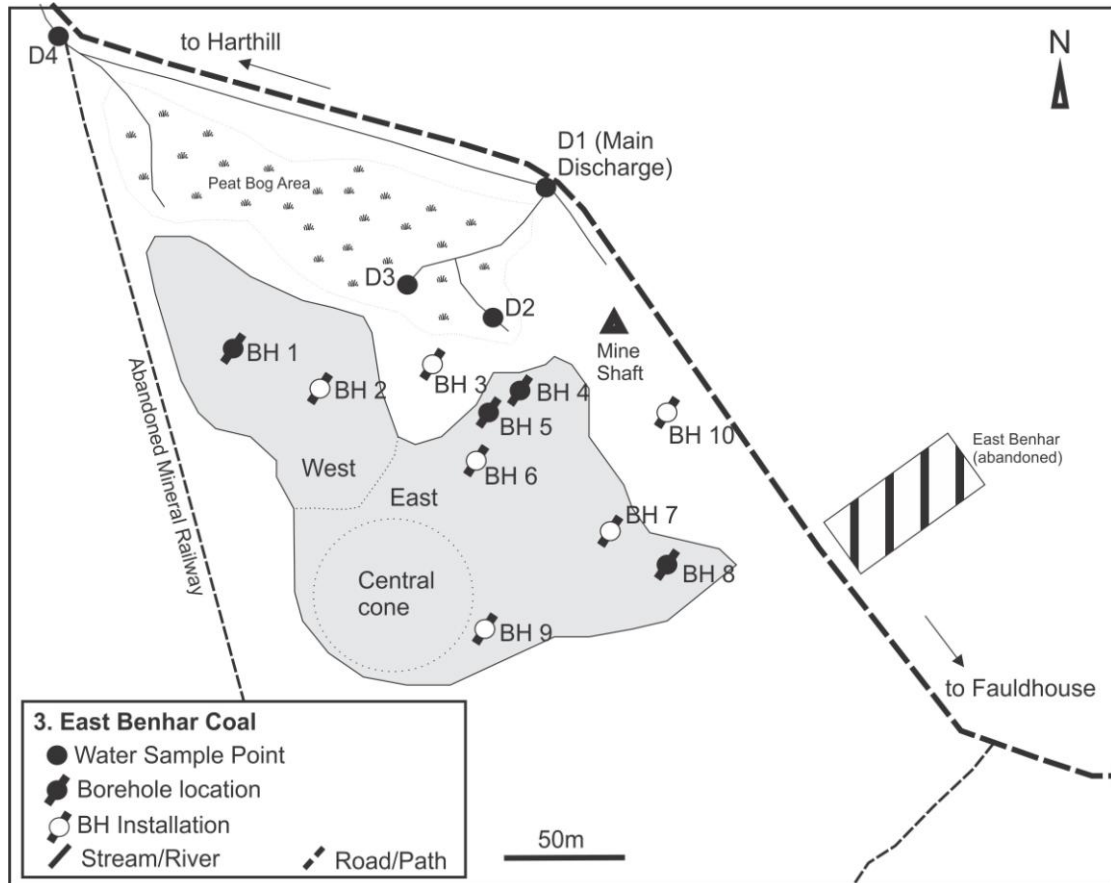


Figure 5.21 - Site 3 site investigation works plan showing the waste pile (grey) and the ten boreholes drilled into the waste and surrounding area as part of the works. Water and discharge sample positions on the main drainage area and associated peat bog area to the north and north west are shown (black circles). The central cone area identified rises approximately 8m above the surrounding lower lying waste pile.

5.6.2 Ground conditions

Site overview

The site comprises of approximately 22,000m² of mine waste of two dominant waste rock lithologies. The north western waste is a dark grey gravely mudstone/shale forming a low lying vegetated mine waste pile 1-2m high; the south-eastern lithology is a light grey to yellow clastic sandstone and mudstone which forms a central cone 6-8m high (Figure 5.21). A single distinct mine water discharge is observed to the north channelled parallel to Harthill road. This discharge is formed from water moving northwards through the waste into a peat bog area which contains low lying reed vegetation. Red/orange ochre deposits are observed in this peat bog area and in the channel next to Harthill road. The mine water discharge converges with road and field drainage to the north and is directed 1) northwards into the River Almond,

along with other mine water discharges in the area, and 2) to the north east into Cultrig Burn which eventually converges with the River Almond.

Intrusive site works

Site investigations at the site involved sampling and borehole installation formed using a handheld window sample rig. A tracked window sample rig was not used due to uneven ground to the west and south of the site and the drainage ditches to the east making access difficult. The handheld equipment was carried by hand over the eastern drainage ditches. Ten intrusive boreholes were formed although refusal occurred in three of these (BH4, BH5 and BH8) at depths less than 1m, six of the boreholes were installed with smaller diameter piezometers (BH2, 3, 6, 7, 9, 10). No boreholes were formed to the south or west of the site because of access issues.

Boreholes in the waste were formed to depths between 2 and 3.8mbgl; a mine waste sample was recovered every 0.25-0.5m. The waste to the north and west although layered and locally variable is described as a weathered dark grey slightly clayey sandy gravel of mudstone and occasional sandstone. There is some evidence of mineral oxidation with occasional red, orange and green oxidation surfaces on gravels. No significant groundwater strike was encountered in this area of the waste, although some layers were moist to the touch. The waste to the east was encountered only as a thin layer of white-brown sandy gravels of sandstone with occasional coal and mudstone in BH's 4, 5, 6, 7, 8 and 9 (Borehole logs are provided in Appendix B). Intrusive investigation could not be undertaken on the central cone due to the angle of the slopes. The waste visible on the cone's surface consists of fine grained yellow to brown sandstone boulders surrounded by fine clayey gravel of sandstone and mudstone.

Boreholes (BH4 and 10) revealed a brown clayey poorly decomposed peat beneath a thin layer of mine waste deposits. The peat layer (0.6-3.4mbgl) is thicker in BH4 than the peat layer (1.5-1.8) in BH10 potentially indicating the unit is thinning towards the east. In both boreholes the peat is underlain by a light grey to brown sandy clay. The superficial geology beneath the waste is similar to that of Site 1,

0.5km to the north, and is consistent with the superficial geology on the 1:50,000 British Geological Survey (BGS) for the area which shows peat on Fauldhouse Moor surrounded (underlain) by Devensian till deposits. The solid geology below the site shown on BGS maps is Scottish Middle Coal Measures underlain by Scottish Lower Coal Measures.

Groundwater

Borehole	GW Strike (mbgl)	Base (mbgl)
BH2	No GW strike	3.0
BH3	1.13	3.5
BH6	Damaged	2.2
BH7	1.1	1.2
BH9	1.1	2.5
BH10	0.35	2.0

Table 5.14 – Groundwater level monitoring from borehole installations at Site 3 on the 02/11/2010. Borehole positions are shown on Figure 5.21

Borehole installations in the mine waste pile at Site3 were monitored on 2/11/2010. Groundwater was encountered at between 1.1 mbgl in BH 7 & 9 on the eastern edge of the waste pile. No groundwater strike was recorded in BH 2. BH3 and BH10 encountered water in the peat surrounding the waste pile. This indicates a limited thickness of perched groundwater within the eastern side of the waste pile but no groundwater in the western side of the waste pile. The peat surrounding the site contains a consistent groundwater body; the boreholes in the peat were more productive during sampling than those within the waste.

5.6.3 Mineralogy

The XRD analysis produced two differing mineralogical assemblages demonstrating the differing observed mine waste lithologies at the site (Table 5.15).

Phase	Formula	Site 3- West				Site 3 -East			
		n	Max	Median	Min	n	Max	Median	Min
Quartz	SiO ₂	10	1.7	0.75	0	7	6	3.9	2.6
Microcline	KAlSi ₃ O ₈					7	11.2	7	3.3
Albite	NaAlSi ₃ O ₈					7	11.3	6	4.3
Orthoclase	KAlSi ₃ O ₈					7	16.4	4.8	1.9
Dickite	Al ₂ Si ₂ O ₅ (OH) ₄	10	30.5	22.4	10.1				
Illite	K _{1.5-1.0} Al ₄ [Si _{6.5-7.0} Al _{1.5-1.0} O ₂₀](OH) ₄	8	48.6	29.1	24.7				
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	10	27.5	23.75	13.7	7	52	34	33
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	10	42.7	18.94	14.82	5	47.7	40.7	35.8
Calcite	CaCO ₃					2	1.9	1.12	0.34
Siderite	FeCO ₃	3	4.08	2.38	1.42	1	4.2	4.2	4.2
Goethite	FeOOH	10	1.57	1.17	0.25				

Table 5.15- QXRD mineralogical analysis results (in wt %) returned by the reitveld analysis from 10 samples from the west Site 3 and 7 samples from the east Site 3 recovered at various depths from boreholes cores.

Benhar west

Benhar west, analysed in 10 samples recovered from BH1 at depths up to 2.25 m, consisted principally of clay and sheet silicate minerals, kaolinite, muscovite, illite and dickite with minor fractions of quartz, siderite and goethite (Figure 5.22). It is therefore similar to the ironstone waste encountered at Site 1 except with no identifiable pyrite or jarosite content. The oxidation minerals observed as red, orange and green crusts during the investigations suggest the presence of an oxidised sulphide mineral, probably pyrite. However, as no pyrite was detected by QXRD this suggests that any pyrite present was at less than the QXRD detection limits of ~1 wt%.

The lack of identifiable calcite or dolomite in the waste indicates limited buffering capacity; the identification of siderite, an Fe carbonate, indicates some capacity but also the coincidental release Fe negating any significant gain in acidity buffering. The weathering of silicate minerals may offer some acid buffering capacity. Since no acid producing minerals were identified in significant quantities, weathering of carbonates and silicates is likely to be facilitated principally by acidity inherent in rainfall.

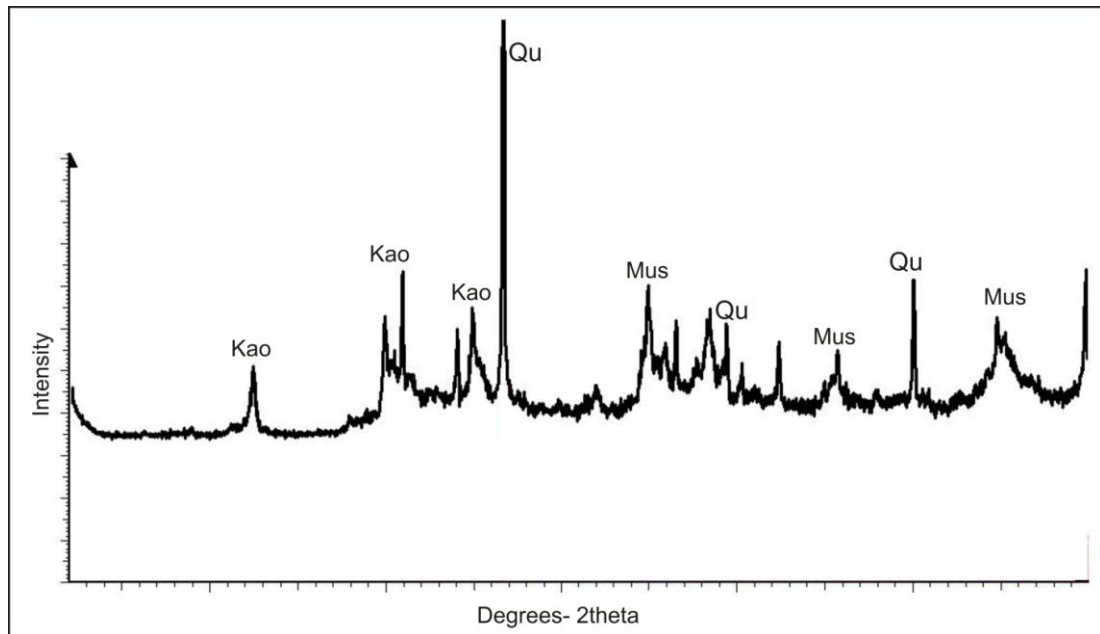


Figure 5.22 - Site 3 Benhar West typical XRD analysis trace returned showing kaolinite – Kao, quartz- Qu and muscovite- Mus diagnostic peaks.

Benhar east

Benhar East, analysed in 8 samples recovered from BH6 and 10 at depths up to 4.0m, consisted principally of sheet aluminium silicates, kaolinite and muscovite, with lesser fractions of quartz and feldspar minerals, microcline, orthoclase and albite. The combined feldspar and quartz content of the lithology, up to 40wt%, indicates the significant clastic, sandstone like, content of the waste. No pyrite or K-jarosite was identified in the waste. Calcite was identified in two samples while siderite was identified in one.



Figure 5.23 - Photograph of the East Benhar mine waste -Heavily vegetated 'older' mine waste in the left foreground with 'newer' conical mine waste behind. Path of old mineral railway on the right

5.6.4 Sampled waters

The principal discharge (D1) at Site 3 was sampled twice; following the intrusive site investigation work on the 01/11/2010 and a year following the works on 09/08/2011, a drainage channel which runs into the peat bog area (D2) was also sampled along with a collection pool (D3) and a downstream sample at the north-west corner (D4). Water samples were also recovered from three boreholes (BH 3, 8+10). The remaining boreholes installation did not contain significant recoverable groundwater. The principle discharge (D1) shows conductivity values of 243-382mS/cm, slightly elevated Fe, up to 1mg l^{-1} , and low sulphate concentrations, SO_4^{2-} , up to 20.8mg l^{-1} , with a slightly acidic pH, 5.9-6.7. The reduced iron species, Fe^{2+} , dominates over the oxidised species, Fe^{3+} . Speciation modelling indicates that FeHCO_3^+ also dominates over the Fe^{3+} species. The main discharge water is classified using the Younger (1995) scheme as 'alkaline and sulphate dominant' in 2011 but chloride dominates in the 2010 water and as HCO_3^- dominant using the Facies Piper groundwater classification convention. Concentrations of Ca (18.2 and 23.8mg l^{-1}), Mg (13.1 and 18.0mg l^{-1}) and bicarbonate, HCO_3^- (99 and 136.7mg l^{-1}) are not considered to be elevated for AMD environments. Speciation modelling on the principle discharge waters indicate that they are over saturated with respect to goethite and some iron oxyhydroxides ($\text{Fe}(\text{OH})_3$). The other surface discharge waters (D2,3,4) sampled at the site show similar chemistry to that of the principle discharge. BH9 shows the highest recorded Fe concentration at the site with Fe^{2+} at 3.4mg l^{-1} .

Location	D1	D1	D2	D3	D4	BH3	BH9	BH10
Description	Main	Main	Site Channel	Surface pool	Downstream			
Date	01/11/2010	09/08/2011	01/11/2010	01/11/2010	01/11/2010	01/11/2010	01/11/2010	01/11/2010
Temp (°C)	7.9	12.2	8.3	9.2	5.2	9.9	9.7	8.2
Eh (mV)	361.9	282	452	343	760	388	315.8	494.4
pH	5.9	6.7	6.0	6.1	6.3	5.7	6.1	5.9
Dissolved Oxygen		10.5						
Conductivity (µS/cm)	382.0	243.0	266.0	374.0	190.0	601	365	289
Ca	18.2	23.8	10.4	22.5	16.8			
Mg	13.1	18.0	3.6	9.4	8.4			
Na	3.9	4.6	3.3	4.6	6.5			
K	42.7	2.7	40.3	41.1	40.2			
HCO ₃ ⁻	99.0	136.7	35.0	119.0	71.0			
Cl ⁻	28.5	5.1	27.7	29.7	29.7			
SO ₄ ²⁻	13.5	20.8	5.2	1.6	10.0	6.31	7.7	28.7
NO ₃ ⁻	1.5	0.5	1.7	2.4	1.1			
Fe _{tot}	0.415	1.010	0.412	0.432	0.589	0.97	3.062	0.256
Fe ²⁺	1.058	<i>0.951</i>	0.301	0.439	0.373	0.179	3.457	0.122
Fe ³⁺	0.000	<i>0.059</i>	0.111	n/a	0.216	0.791	n/a	0.134
Mn	0.280	0.055	0.010	0.235	0.021	0.754	0.232	0.035
Al	0.067	0.074	0.219	0.005	0.187	0.723	2.080	0.138
SiO ₂	9.24	8.32	10.40	8.00	9.90			
Balance	9.0	2.8	15.3	5.5	12.9			
WATEQ4F Speciation Model								
Phases								
Fe(OH) ₂ .Cl.3	-	6.67						
Fe(OH) ₃	-	1.91						
Goethite	-	7.32						
Jarosite (SS)	-	-2.23						
Jarosite-K	-	-3.39						
Jarosite-Na	-	-7.02						
Siderite	-7.1	-0.6						

Table 5.16 - Analysis data from sampled waters at Site 3- East Benhar, the sample location corresponds to those shown in Figure 5.21. All units in mgL⁻¹ unless otherwise stated. n/a= not applicable, S.I. = saturation index. Where the Fe²⁺/Fe³⁺ speciation has been determined by WATEQ4F speciation modelling (as opposed to on site preservation) this is written in *italics*.

5.6.5 Modelling results

Using the QXRD mineralogical assemblages returned for the site in the inverse modelling function in PHREEQC proved problematic. In the first instance, a solution could not be returned because Mg in discharge waters had no source mineral, unlike in other site models where dolomite acted as the Mg source. Although no dolomite was identified in the XRD analysis the decision was made to include it as a phase in the inverse model. It is possible that Mg could have been sourced from amorphous phases, illite (as it is often found in the mineral structure, although it is not included as a constituent in the formula used in PHREEQC) or ankerite. However, as no ankerite was identified in the XRD analysis and PHREEQC could not represent illite or amorphous phases as Mg sources, dolomite was instead included. Pyrite was also included because of field evidence of limited Fe and SO₄ precipitate formation on the waste at depth and the ochre formation observed at the site discharge.

Following the addition of dolomite the model balance between Ca, Mg and dolomite could still not be achieved until the uncertainty for final mine water solution, D-2011, was increased to 0.19. For D-2010 the uncertainty was increased to 0.45 without the return of a solution, the decision was made to not increase the uncertainty further. Although the uncertainty is a constraint of analytical error for each of the input/output chemical solutions it also dictates how the model is able to vary each chemical element in the simultaneous linear mass balance equations which is used to achieve a solution in the inverse function. Therefore, increasing the uncertainty value for the minewater solutions to 0.19, or 19%, means the solution returned, while explaining the water chemistry evolution can not be considered to be an accurate representation of site geochemistry.

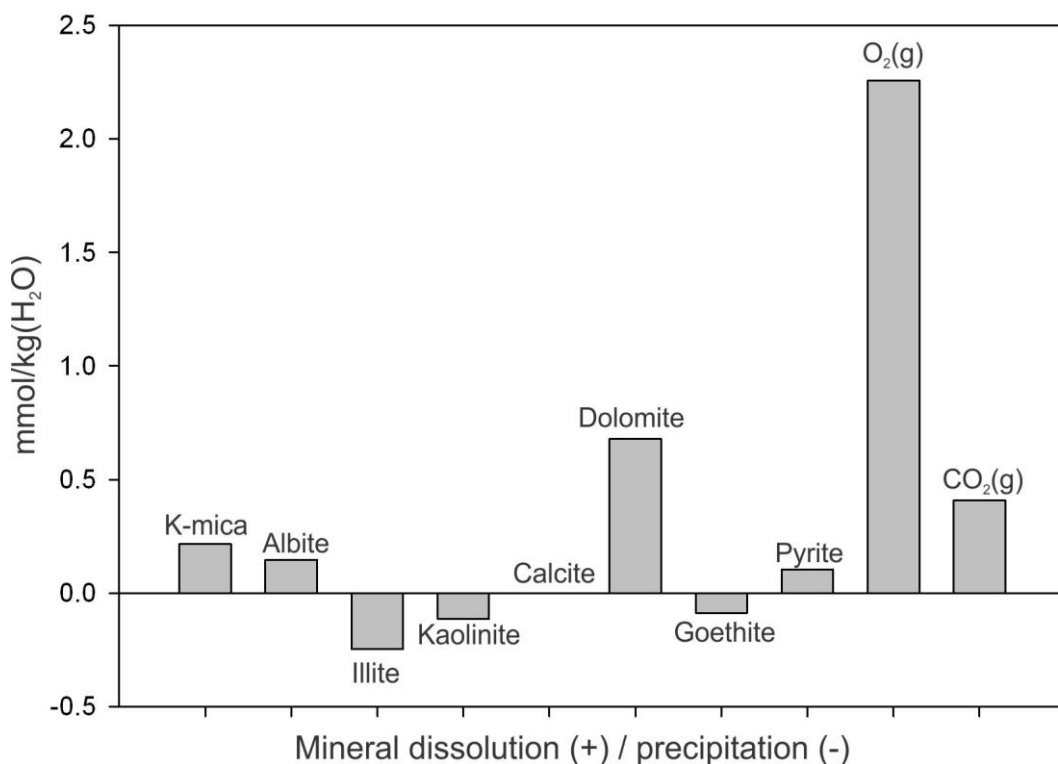


Figure 5.24 - PHREEQC inverse model results returned for the D1-2011 discharge sample when using an uncertainty value of 5% for rainwater and 19% for the discharge sample. The mineralogical phases included in the model were identified by QXRD analysis. The inverse model balances the difference between rainwater entering the site and the discharge chemistry by the dissolution or precipitation of phases from the known mineralogical assemblage.

Three solutions were returned for the D1-2011 inverse calculations of which one solution was considered reasonable. The two eliminated solutions involved the dissolution of unfeasibly large amounts of siderite. In reality it is likely siderite dissolution may exert significant control of the discharge water evolution, however, the solutions returned by PHREEQC showed an order of magnitude greater siderite dissolution than any other mineral phase, and this was balanced in the model by an almost equally large dissolution of goethite. Hence these solutions were discounted. The remaining solution shows dolomite to be the principal control on the discharge water with secondary influence from aluminium silicates, pyrite and goethite precipitation. The sum of residuals for the selected solution is 5.20.

5.6.6 Site discussion and conceptual model

Waste origin

Site and historic investigations undertaken on the mine waste site at East Benhar indicate that the waste consists of two different mine waste types.

- The western waste, associated with the Fallahill colliery to the south, shows an argillaceous signature dominant in dickite, illite, kaolinite, and muscovite, consistent with it being derived from mudstones and shales in the Scottish Coal Measures.
- The eastern waste, associated with the Behar mine, is more arenaceous in nature containing higher quantities of quartz and feldspar minerals, indicating the Benhar mine extracted more sandstone dominant material.

Neither of the waste assemblages contained significant identifiable pyrite, jarosite or any other significant acid producing mineral (sulphide or AGS). Some evidence of sulphide oxidation was observed during intrusive works in the form of precipitate minerals on the edge of waste fragments, this was confirmed by up to 1.5wt% goethite QXRD identification.

Site hydrogeochemistry

Groundwater monitoring shows some evidence of a perched groundwater aquifer in the eastern side of the site, which is probably in contact with the groundwater in the surrounding peat encountered in BH3 and BH10.

The Fe concentrations in the discharge, D1, and BH9 are indicative of limited Fe mobilisation at the site, possibly related to pyrite oxidation or goethite and siderite weathering reactions. The geochemistry operating at the site is likely to be influenced by waters moving through the peat bog area, which may promote sulphate reduction as waters show low Eh (282-361 mV) and peat is general reducing in nature. This scenario is analogous with passive anaerobic wetland mine water treatment where

anoxic conditions and the abundance of carbon in the peat encourage sulphate reduction (Hedin et al. 1994).

The positive identification of Fe precipitates at the site also indicates the oxidation of Fe in discharge waters as they emerge at surface in the peat bog area and at the discharge point. The slightly reduced pH of discharge waters could also be considered an indication of limited acid production although the Sourhope Scottish rainwaters chemistry indicates a pH of 5 (Table 5.4).

Discharge water evolution

As stated in Section 5.6.5 the inverse model solution returned for the site may not best represent the true evolution of water chemistry between rainwater input and discharge associated with the returned QXRD mineralogical phase assemblage. A possible cause of this maybe related to the peat bog area through which the waters are discharged prior to sampling. The model solution indicates relatively low dissolution/precipitation operating at the site:

- Pyrite oxidation (0.105mmol/kg) is of limited influence on the discharge chemistry but its inclusion accounts for the Fe and SO₄ concentrations recorded in the D1- 2011 water. Since pyrite is not identified in the QXRD the limited influence of pyrite seems reasonable.
- Goethite precipitation (-0.08mmol/kg) which is confirmed by the identification goethite in the waste mineralogical assemblage and by the Fe precipitates at the discharge point, acts as a sink for released Fe.
- Dolomite (0.62mmol/kg) and silicate buffering (K-mica 0.2mmol/kg and albite 0.146mmol/kg) are the dominant controls on water chemistry evolution. The non-identification of dolomite in the waste mineralogy is, therefore, problematic.
- Consumption of O₂ (0.4mmol/kg) and CO₂ (2.02mmol/kg) are related to limited pyrite oxidation and goethite precipitation as well as the bicarbonate (HCO₃⁻) dominant signature of the discharge water.

In general the model solution is considered to be a poor representation of the actual site geochemistry. A possible explanation for this is that investigation, which although thorough was not exhaustive, simply did not identify the full mineralogical assemblage at the site. Other studies have suggested ankerite dissolution, which acts as a carbonate buffer and Fe source, to be significant in controlling mine water chemistry (Younger 2004). Furthermore, although PHREEQC had problems in returning feasible solutions involving siderite, it is considered that siderite is likely to offer significant control over the site geochemistry. These findings indicate that the application of PHREEQC to complex mine waste scenarios is of limited use without site investigations which allow full conceptualisation of all the possible water evolution pathways.

Potential environmental impact

The variable nature of the discharge water between sulphate dominance and chloride dominance make interpretations using the Younger (1995) scheme difficult.

- Discharge waters, D1, have limited potential to impact the surface or groundwater water environment, with only the slightly elevated levels of Fe being of any concern.
- The D4 sample which is ~200m downstream of D1 and shows Fe at ~0.5mg/l, a concentration not considered to result in any notable adverse environmental impacts. Fe precipitates generally only form in river waters at above 1mg/l Fe. In the surface water environment the discharge waters therefore only produce localised impacts on water quality in close proximity to the site.
- In the groundwater environment the direct release of Fe from these waters, possibly via the former shaft at the site, is considered to have the potential for greater impact than surface waters. The Fe concentrations in boreholes suggest there may be movement of contaminants in perched groundwaters. However not in BH 10, closest to the former mine shaft.

In summary the potential impact on the water environment associated with discharge of waters at the site is considered to be low, principally due to a low acid mineral content and the discharge arrangement, passing through a peatbog reed bed area.

Conceptual models

Figure 5.25 and Table 5.17 show visual and descriptive conceptual models for Site 3 constructed based on the observations and interpretations outlined above.

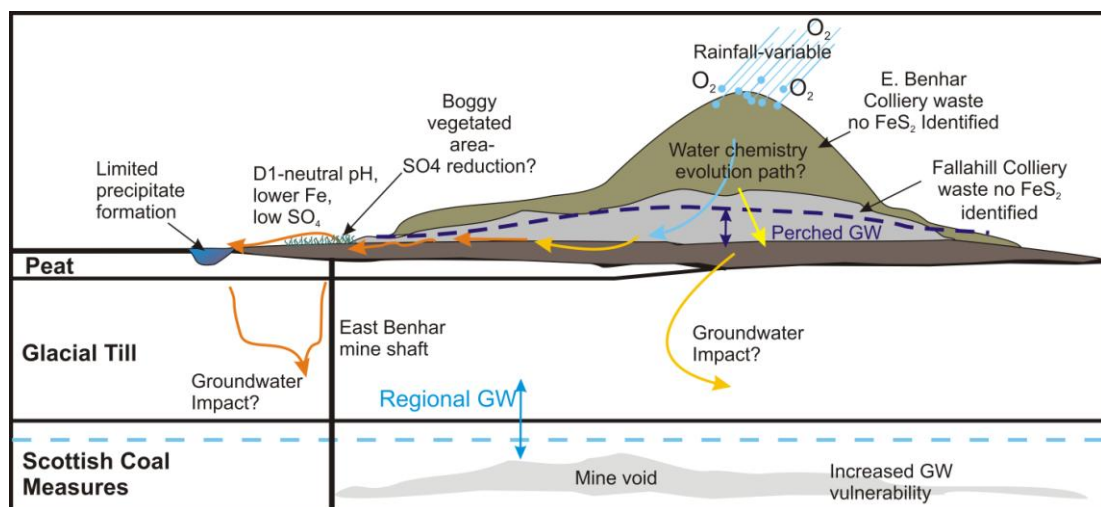


Figure 5.25 - Site 3 visual conceptual diagram indicating the main water chemistry evolution pathway between rainfall water and mineralised discharge water. Also shown is the peat bog area to the left which is thought to complicate the water evolution pathway. The two separate waste types which comprise the site are also shown.

Table 5.17 - Site 3 descriptive conceptual model

SOURCE		Identification		Description
		Identified	Identifier	
Pyrite		No	XRD	1wt% detection limit. Possible at below detection, some visual evidence of precipitate minerals
Secondary AMD salts		No	XRD	1wt% detection limit. Possible at below detection, some visual evidence of precipitate minerals
Carbonates (source buffer)		Limited	XRD	Calcite at 1.9wt% in one sample and visually identified in some other traces. No Dolomite.
Silicates (source buffer)		Yes	XRD	Feldspar and sheet aluminio silicates at high abundance
Ankerite/siderite		No/yes	XRD	Not fully identified by SI but are considered to be the most likely source of Fe and Mg. Hence the issues with accurate model solutions
PATHWAY				
Discharge Chemistry	pH	5.9-6.7	Water analysis	
	Fe	1 mg l ⁻¹	Water analysis	Indication of limited FeS ₂ oxidation. Probably also sourced from Fe carbonate dissolution
	Metals	Yes, low	Water analysis	Need to consider relative impact to receptor
Human Ingestion		Possible-limited	Site observation	The site is naturally heavily vegetated. The central cone has only limited vegetation.
Superficial Geology		Peat	SI	Some slightly elevated Fe. 1-2m thick
		Glacial clays	SI	Sandy clays-generally low K. Significant potential for downward water movement due to heavily mined area.
Solid Geology		Scottish Coal Measures	BGS Maps	Moderate to high K, significant potential for mine void increasing groundwater vulnerability
RECEPTOR				
Surface Water		Yes- limited		Fe precipitates identified in central drainage pool and at discharge point. Impact is likely to low.
Groundwater		Limited		Possible direction contamination to regional groundwater beneath the site due to historic shaft- high groundwater vulnerability due to mine void and shafts.
Human Health		Limited		Limited impact on water wider environment. Possible but limited dust inhalation

5.7 Site 4 Hermand Oil Shale

Site 4 is located at NT 0290 6255, approximately 1.2km SE of the town of West Calder in West Lothian. It can be accessed via a farmer's track to the east of the B7008 between West Calder and Harburn. To the immediate east of the waste pile, in the adjacent field, once stood the Hermand Oil Shale works, no evidence of this remains at the ground surface. To the north and west, close to the Harwood water are the former mine entries for the mine which provided raw oil shale to the oil shale works.

5.7.1 Site history

The Hermand Oil Shale waste, south of West Calder, was associated with the Hermand Oil shale works and historic mine. Records state that the oil works was opened in 1883 but demolished in 1894 leaving behind the waste (Hermand Oil Company Report 1894). This waste is unlike the other mine wastes investigated (Site 1-3); it is principally the waste product of an industrial scale chemical process to extract oil from the oil shale mineral deposit, post mining, at surface in the former Hermand Oil Works (Figure 5.26).

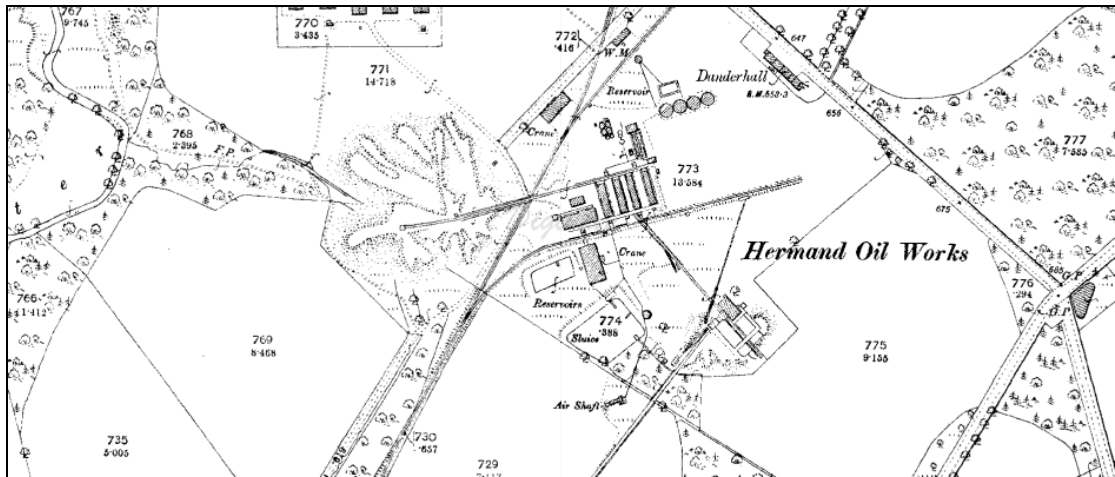


Figure 5.26 - Historic Map of the Hermand Oil Shale Waste- 1st Edition 1894 County Series 1:2500- Showing oil shale mine waste and associated 'Hermand Oil Works' with the Harwood water to the west (Date source- National Library of Scotland)

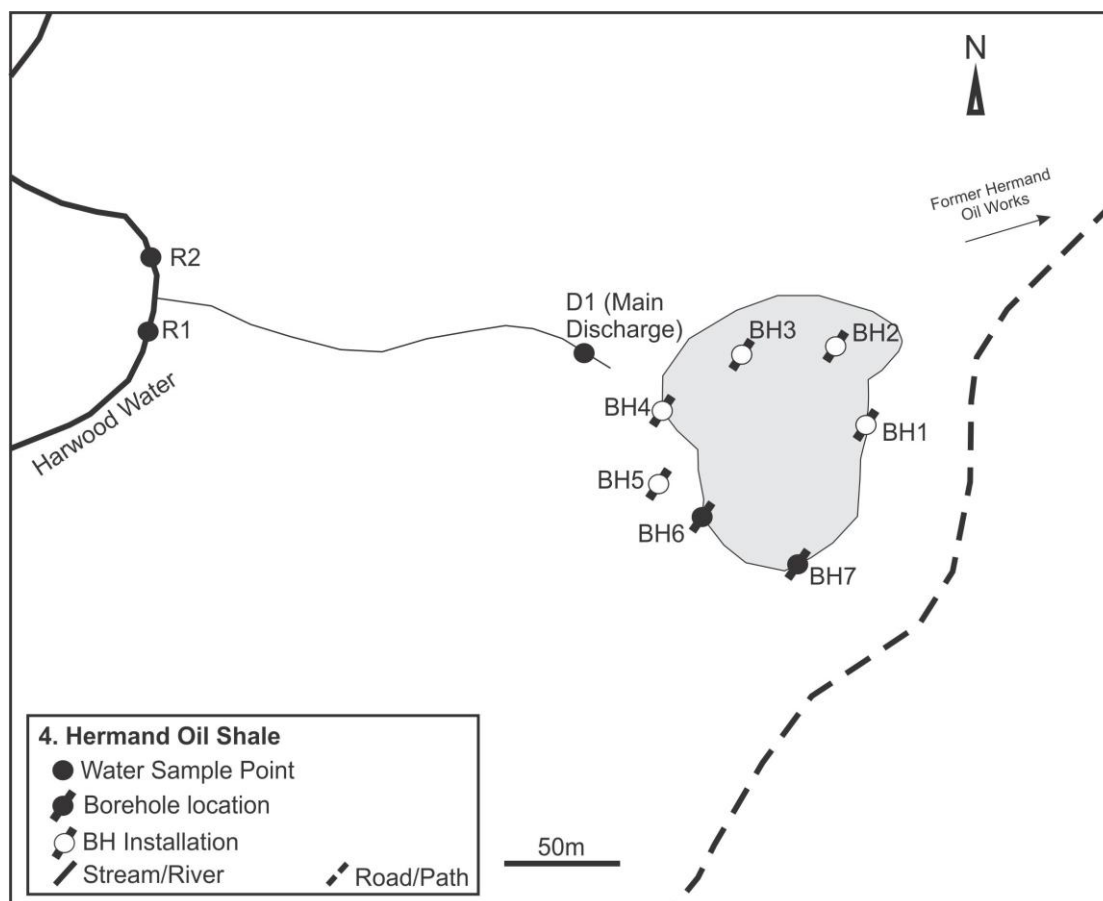


Figure 5.27 - Site 4 site investigation works plan showing the waste pile in grey and the seven boreholes drilled into the waste and surrounding area. Also shown is the main site discharge (D1) flowing into the Harwood water and the water sampling points. To the west of the waste pile, just outside the extent of the plan, stood the former Hermand Oil Shale Works.

5.7.2 Ground conditions

The waste pile consists of, approximately 11,000m², orange red to pink, occasionally black, oil shale processing waste together with a fraction of black mine waste, probably related to mine development at the Hermand mine to the north west. The site contains one main leachate discharge stream (the term ‘leachate’ is used here because it is considered that the majority of the waste is industrial process waste and not ‘true’ mine waste) to the west which discharges into the Harwood Water. Site investigations revealed that this discharge shows significant flow; potentially more than can be attributed to the mine waste alone, and is also likely to incorporate a significant component of field drainage as well as potentially impacted mine waters from the waste pile. It is also possible that the field drainage is impacted by

subsurface mine waters from local oil shale mines. Evidence of iron precipitates are observed on the stream bed of this discharge, close to where it converges with the Harwood Water, these could be related to the mine waste as well as other deeper oil shale mine waters which may be incorporated into the field drainage.

Intrusive site works

The mine waste itself is between 8-10m in height at its highest point, relative to the surrounding ground level. Boreholes formed around the edges of the mine waste revealed that the waste extends outwards and downwards below the apparent surface level of the surrounding field to depths of 2.5 mbgl.

Site investigations at the site involved sampling and borehole installation formed using a tracked Dando windowless sampler in addition to a number of hand dug trail pits in the central region of the site. Seven intrusive boreholes were formed, two on the northern flanks of the raised waste area and five surrounding waste flanks. Five of the boreholes (BH1-5) were installed with smaller diameter piezometers

Boreholes 2 and 3 were formed to depths of 7 and 6 mbgl respectively, and as such penetrated the entire depth of the waste into the underlying superficial geology. The waste in these boreholes consisted of layers of sandy to very sandy fine to coarse gravel of friable variably coloured processed and unprocessed oil shale, with some layers of more clay dominant material and occasionally broken cobbles of larger oil shale fragments. The oil shale colour ranged from black, thought to be raw (unprocessed) oil shale, through shades of brown, orange, pink, red and beige. Where the oil shale is black some surfaces show limited evidence, compared to the other mine waste sites, of red orange oxidation staining, presumably from goethite, jarosite or iron oxyhydroxide precipitation. (Borehole logs are available in Appendix B) The distinct coloured layers of the waste could also be observed from excavations in the edges of the waste made by the farmer who owns the field in which the waste sits (Figure 5.29).

The southern tallest side of the waste pile could not be accessed with the sampling rig, partly due to the angle of the waste and partly due to the fore mentioned excavations making the waste appear unstable. This central area also shows a more ‘rock like’ structure on its flanks. This is a common feature of oil shale waste and investigations into the history of the oil shale processing technology suggests this feature is the result of the waste being over heated in the shale oil extraction retort causing the oil shale fragments to fuse (see Chapter 3).

The remaining boreholes formed around the edges of the main waste pile revealed oil shale waste below the ground surface to depths between 1.4mbgl(BH6) and 2.5 mbgl(BH5). Below the surrounding subsurface waste was generally a thin layer of ‘re-worked’ brown grey sandy clay containing fragments of black and orange red oil shale waste which gave way to natural grey brown sandy clay, which in BH7 became dark grey firm sandy clay. The base of this clay was not encountered, although in BH6 the clay became increasingly gravely with gravels of sandstone and mudstone which may represent the geologically weathered surface of the under lying solid geology. The solid geology is encountered close by; where the site discharge and adjacent Harwood Water cuts down into the sandstone and mudstones of the solid geology. The investigation observations are consistent with the superficial and solid geology on the 1:50,000 British Geological Survey (BGS) map for the area which shows Devensian till deposits underlain by the Hopetoun member and Binny Sandstone of the West Lothian Oil Shale Formation.

Groundwater

Borehole	GW Strike (mbgl)	Base (mbgl)
BH2	No GW strike	3.0
BH3	No GW strike	3.0
BH4	No GW strike	4.0
BH5	No GW strike	4.0
BH7	3.4	3.5

Table 5.18 - Groundwater level monitoring from borehole installations at Site 4 on the 26/11/2010. Borehole positions are shown on Figure 5.27

Borehole installations in the mine waste pile at Site 4 were monitored on 26/11/2010. Groundwater was encountered only in BH7 as a thin layer perched directly on top of the underlying superficial geology. No definite groundwater strikes were recorded in other boreholes although the bases of some were found to be moist.

5.7.3 Mineralogy

Phase	Formula	n	Max	Median	Min
Quartz	SiO ₂	19	47.1	30.3	13.8
Microcline	KAlSi ₃ O ₈	2	4.3	3.6	2.9
Albite	NaAlSi ₃ O ₈	19	4.9	2.4	0
Anorthite	CaAl ₂ Si ₂ O ₈	18	12.4	7.9	0
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	16	10.9	1.0	0
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	19	53.9	18.6	2.7
Calcite	CaCO ₃	4	1.1	0.7	0.5
Dolomite	(CaMg)(CO ₃) ₂	16	3.4	0.9	0.4
Hematite	FeO ₂	17	13.2	8.3	1.4
Pyrite	FeS ₂	2	0.7		0.3
Siderite	FeCO ₃	2	0.5		0.3
Magnetite	Fe ₃ O ₄	1	12.0		
Cordierite	(Mg,Fe) ₂ [Si ₅ Al ₄ O ₁₈].nH ₂ O	13	16.9	4.4	0.8
Mullite	3Al ₂ O ₃ .2SiO ₂	12	35.6	28.1	20.7

Table 5.19 - QXRD mineralogical analysis results (in wt %) returned by the reitveld analysis from 19 samples from Site 4 recovered at various depths from boreholes cores.

QXRD mineralogical analysis revealed the oil shale waste consisted principally of quartz, feldspars, muscovite, kaolinite and hematite with minor fractions of carbonate minerals- dolomite and calcite (Table 5.19). Two of the samples (BH4- 2.2mbgl, BH2, 3.6mbgl) recovered from black oil shales in the waste showed a mineralogy indicative of raw oil shale or 'blaes' which was lacking in hematite or cordierite and consisted predominantly of aluminosilicate minerals, quartz and minor fractions of

siderite and pyrite. (BH2, 3.6mgbl, also contained a significant proportion of magnetite).

Identification of illite, in the waste, was troublesome as it was difficult to separate the signatures of illite with that of muscovite, mica and also kaolinite. This problem was also alluded to by Louw and Addison (1985) where the identification of 'illite-smectite mixed layer silicates' in the un-processed oil shale was also difficult. The decision was made to exclude illite from the Rietveld analysis because when included, illite appeared to preferentially dominate the trace by reducing the muscovite and kaolinite contents. However, the overall silicate mineral content of the traces remained constant; therefore, the combined muscovite and kaolinite contents reported here should be considered as overall undifferentiated aluminium silicate clay mineral content with an indeterminate proportion of illite.

In some layers significant quantities of cordierite and mullite were recorded, up to a maximum of 17wt% and 35wt% respectively. These minerals are not common in mine wastes as they are formed in high temperature environments; here they are likely to have been formed in the industrial heating processing of the oil shales. The hematite content varied from ~1 to 14wt% and is thought to be the responsible for the variable colours of the waste layers (Figure 5.28).

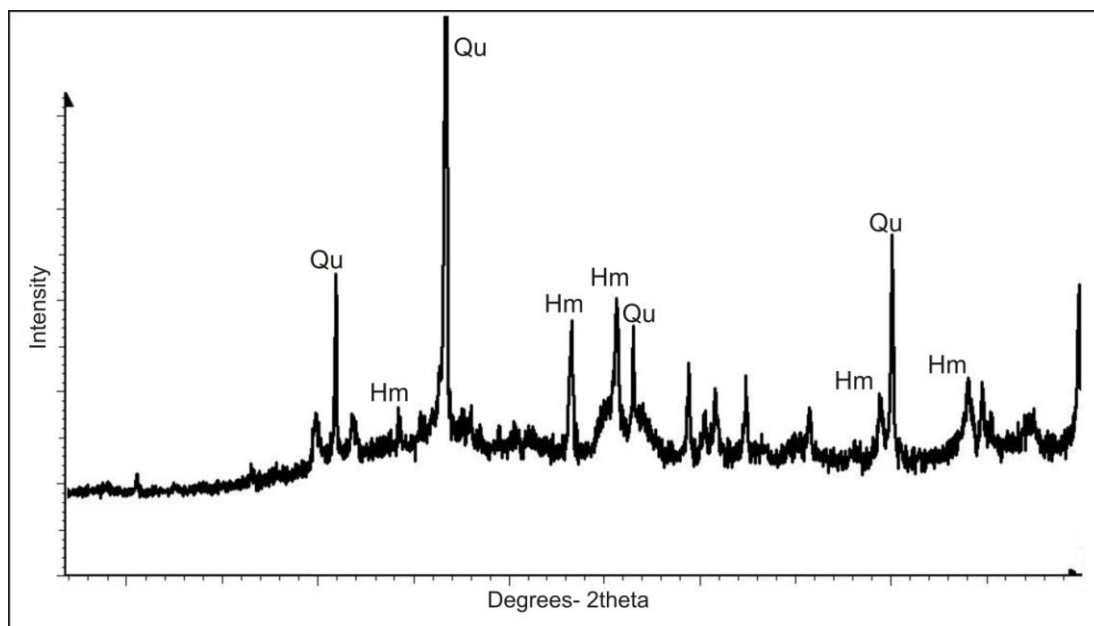


Figure 5.28 - Site 4 XRD trace showing hematite –Hm and quartz- Qu diagnostic peaks. The distinct hematite identification is consistent with the general red coloration of the majority of the processed oil shale wastes.

Some pale yellow precipitates were observed on the stream bed of the principal discharge from the site prior to its confluence with Harwood Water. None of these precipitates were recovered from XRD analysis but are thought to be ochres formed from Fe precipitation.



Figure 5.29 - Photograph showing of excavated side of Hermand oil shale waste. The different layers of orange, red, beige and black oil shale waste are shown. The black wastes are likely to represent unprocessed oil shale which may contain pyrite and act as a source of Fe in discharge waters. The red coloration of the rest of the waste is due to the variable hematite content which is formed via the industrial processing due to oxidation of the iron content of the oil shale.

5.7.4 Sampled waters

The principal discharge (D1) at Site 4 was sampled twice; following the intrusive site investigation work on the 26/11/2010 and a year following the works on 03/08/2011, the Harwood Water was sampled upstream (R1) and downstream (R2) of the point where D1 discharges to the river. No recoverable water was encountered in any of the borehole installations.

The principle discharge (D1) shows conductivity values of 353-527mS/cm, elevated iron, Fe-up to 2.4mg l^{-1} , low sulphate concentrations, SO_4^{2-} up to 26.3 mg l^{-1} , and a slightly acidic to near neutral pH – 5.9-6.7. The reduced iron species, Fe^{2+} , dominates over the oxidised species, Fe^{3+} in the D1-2010 sample while the opposite is true in the D1-2011 sample. Speciation modelling indicates that FeHCO_3^+ and Fe(OH)^{2+} iron species are also significant. The main discharge water is classified using the Younger (1995) scheme as ‘alkaline and sulphate moderate’ and as Ca- HCO_3^- dominant using the Facies Piper groundwater classification convention. The chloride, Cl, content of the D1 water differs significantly between the 2 sampling dates. The levels of Fe recorded in discharge waters can be considered to be environmentally significant and are higher at 2.4mg l^{-1} in the more sulphate dominant sample D1-2011.

Location	D1	D1	R1	R2
Date	26/11/2010	03/08/2011	26/11/2010	26/11/2010
Temp (°C)	5.5	13.0	3	3.5
Eh (mV)	254.4	386.6	306.3	332
pH	6.8	6.5	7	7.2
Dissolved Oxygen		9.8		
Conductivity (µS/cm)	527	353.0	171.6	177.9
Ca	64.8	51.4	19.2	20.4
Mg	10.94	8.46	3.68	3.84
Na	13.3	14.3	5.6	5.8
K	62.47	23.77	3.34	2.64
HCO ₃ ⁻	229	155	53	58
Cl ⁻	42.94	15.4	7.9	6.7
SO ₄ ²⁻	23.15	26.2	11.1	11.6
NO ₃ ⁻	6.41	9.68	1.7	1.7
Fe _{tot}	1.38	2.4	1.36	1.34
Fe ²⁺	1.13	0.95	n/a	1.54
Fe ³⁺	0.25	1.45	1.36	n/a
Mn	3.29	0.463	0.183	0.214
Al	0.03	0.154	0.15	0.15
SiO ₂	9.16	9.41	2.6	2.62
Balance	7.83	11.32	11.2	10.9
WATEQ4F Speciation Model				
Phases	S.I.	S.I.		
Fe(OH)2.Cl.3	7.94	7.68		
Fe(OH)3	2.94	2.72		
Goethite	8.08	8.17		
Jarosite (SS)	1.58	1.74		
Jarosite-K	0.17	0.81		
Jarosite-Na	-4.46	-3.26		

Table 5.20 - Analysis results of sampled waters from Site 4- Hermand Oil Shale, the location of each of the samples relates to the positions shown in Figure 5.27. All units are in mgL⁻¹ unless otherwise stated. n/a= not applicable, S.I. = saturation index. Where the Fe²⁺/Fe³⁺ speciation has been determined by WATEQ4F speciation modelling (as apposed to on site preservation) this is written in *italics*.

Concentrations of Ca (51.4 and 64.8mgL⁻¹), Mg (8.46 and 10.94mgL⁻¹) and bicarbonate, HCO₃⁻ (155 and 229mgL⁻¹) are moderately elevated. The discharge waters also contain unusually high levels of potassium, K⁺, at 62.47mgL⁻¹ in the 2010 sample.

The D1 discharge contains relatively high levels of nitrate, NO_3^- , at $6.41\text{--}9.68\text{mg l}^{-1}$. Speciation modelling on the principle discharge waters indicate that they are oversaturated with respect to goethite, some jarosite phases and iron oxyhydroxides ($\text{Fe}(\text{OH})_3$).

The river water R1, which is upstream of the site discharge, is Ca-HCO_3 dominant and shows lower concentrations of all the major ions than the discharge water, although it contains similar Fe at 1.36mg l^{-1} .

5.7.5 Modelling results

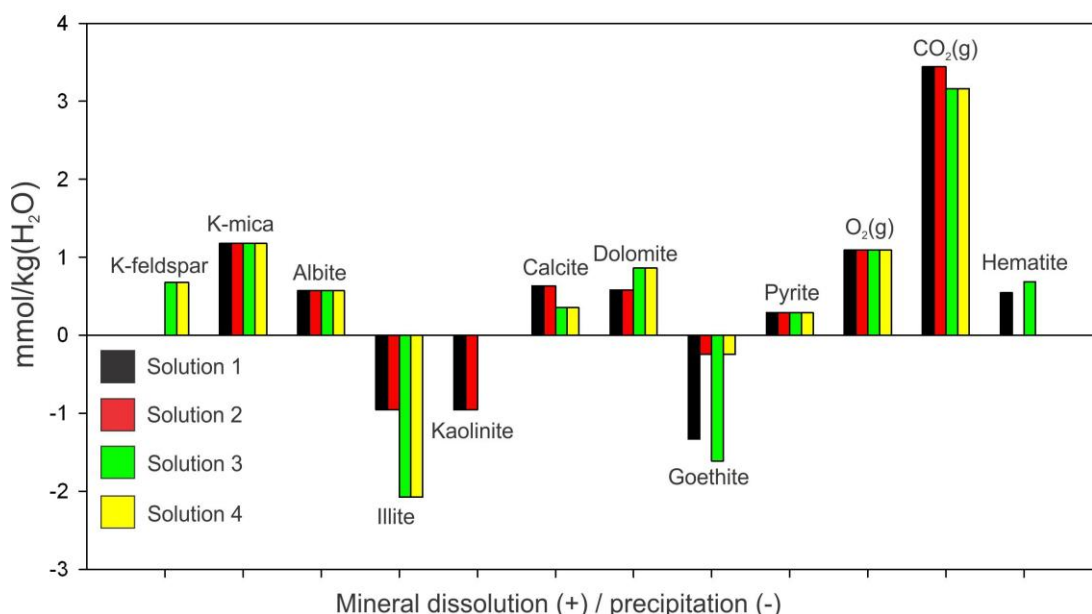


Figure 5.30 - PHREEQC inverse model results returned for the D1-2011 discharge sample when using a global uncertainty of 5%. The mineralogical phases included in the model were identified by QXRD analysis. The inverse model balances the difference between rainwater entering the site and the discharge chemistry by the dissolution or precipitation of phases from known mineralogical assemblage.

Four solutions were returned for the D1-2011 inverse calculations displayed in Figure 5.30. D1-2010 was run under the inverse function in PHREEQC but the 3 solutions returned were considered unfeasible because the waters were balanced by unrealistically large amounts of hematite dissolution and goethite precipitation.

5.7.6 Site Discussion and Conceptual Model

Waste Origin

The orange red burnt shales in the waste pile are processed oil shale from the shale works while the black shale is likely to originate directly from the mine. The predominant red orange colour of the processed oil shale waste is a feature consistent with the numerous oil shale wastes found across West and Mid-Lothian (Winter 2000, Harvie 2005). QXRD analysis suggests that the colour of the processed oil shale is likely to be related to the hematite (Fe_2O_3) content of the waste which is a signature of the heat processing of the waste used to extract oil from the raw oil shale (see Chapter 3).

The black layers of waste identified are probably poorly processed or un-processed oil shale or blaes. This seems logical since no ‘overburden’ mine waste piles associated with the mine progression at the associated Hermand Mines are observed in the area. Inferior oil shale mine development waste which was not deemed suitable for processing appears to have been discarded along with the processed oil shale.

Site Hydrogeochemistry

- The non-identification of a significant water table at the site in installed piezometers, which penetrate the full waste thickness, suggests that waste is free draining; this is a common feature of other oil shale sites which has been suggested in other studies (Harvie 2005).
- Influence of the waste mineralogy, processed (red orange) and unprocessed (black), on the discharge waters at D1 is considered to be periodic as the site does not retain a significant store of water to be discharged during dry periods.

- The discharge chemistry at D1 differs significantly between the 2010 and 2011 samples a possible indication of variably sourced waters.
- Elevated nitrate concentrations at D1 are not associated with the waste mineralogy, as oil shale waste is generally nitrate poor (Harvie 2005), and are probably associated with agricultural field drainage from surrounding areas.
- Pyrite was only identified at very low quantities in black oil shale horizons in the waste. This pyrite contain may account for the Fe concentrations in D1. Another possible source is from mine waters upstream of the site which may contribute to the D1 discharge.
- The variability and relatively high Cl content in the D1 waters may be related to the flushing of pore waters contained within the black oil shale/blaes (See Chapter 4). However, a corresponding high Na content would also be expected which is not seen in the sample chemistry.

Discharge Water Evolution

The PHREEQC inverse model was run using the site mineralogy with the inclusion of pyrite although it was only found to be a minor fraction in 2 of the black shale samples. The model for D-2011 produced four solutions of which two included carbonate, silicate and pyrite dissolution while the other solutions also included hematite:

- In general influence of dissolution reactions was low, at or below 1mmol/kg for each phase.
- The inclusion of hematite dissolution is significant because it indicates that Fe precipitates maybe produced by weathering of hematite in the oil shale. In practise it is unlikely hematite acts as a significant source of Fe due to its mineral stability requiring a significant excess of acidity to mobilise Fe (Chapter 3).

- All the solutions indicate the dissolution of K-mica (1.18mmol/kg) and albite (0.58mmol/kg) account for the release of Na^+ and the precipitation of illite and kaolinite.
- Calcite and dolomite dissolution occur in all solutions; dolomite dominates in solutions 3&4(calcite-0.64, dolomite-0.58mmol/kg) while calcite dominates in solution 1 & 2 (calcite-0.28, dolomite- 0.88mmol/kg). This accounts for the Ca, Mg in discharge waters together with the consumed CO_2 gas which produces HCO_3^- alkalinity. The amount of CO_2 consumed differs between model solutions.
- The carbonate dissolution reactions consume acidity in rainwater, which enters the model/waste at pH-5, as well as consuming acidity released by the oxidation of pyrite (0.29mmol/kg). As with sites 1 and 2 the pyrite oxidation is balanced by goethite precipitation (-0.25-1.33mmol/kg) resulting in the Fe- SO_4^{2-} ratio of 25.8 (Fe-1.01, SO_4^{2-} -26.1mg/l).

In general the Fe and SO_4 observed in waters suggest the black oil shales in the waste are the principal control on the water evolution although the carbonate and aluminosilicate content of the processed oil shales maybe significant. The volume of the discharge water at the site does indicate that the waste mineralogy is only likely to be of partial control on the observed chemistry of the waters, this is supported by the non-return of a solution for D1-2010 discharge water. The model solutions offer some insight into the possible dissolution/precipitation reactions at the site however upstream agriculturally and mine sourced water are considered to also influence the D1 water chemistry.

Potential Environmental Impacts

Modelling and interpretations on the D1 water chemistry suggest that the oil shale waste is of partial influence on the discharge chemistry. The presence of red orange Fe precipitate deposits although limited in volume suggests the potential for some adverse impacts on water quality.

- The classification of the D1 water as ‘*alkaline and sulphate moderate*’ indicates it has a relatively low potential to impact the quality of surface water environment. The elevated Fe concentrations and precipitate could still be of concern when discharged to pristine surface water. The R1 and R2 samples indicate that the Harwood water contains elevated concentration of Fe both before and after the input of the D1 discharge. Therefore, the input of D1 makes no significant increase in Fe levels in the river, in fact the Fe concentration between R1 and R2 is actually reduced. This reduction is likely to be an artefact of the variability inherent in sampling a flowing stream.
- As the D1 discharge is of little influence on the already elevated concentrations of Fe in Harwood water the impact of the site itself, which is probably, only of partial influence on the D1 chemistry, also poses only limited threat to the Harwood water quality.
- The former Hermand Oil Shale works may pose some environmental risk to the Harwood water due to the potential for hydrocarbon contaminated land; however, no assessment of hydrocarbon contamination was made during the site investigation works.
- Elevated concentration of major ions, particularly Cl, may influence the chemistry of Harwood water. Indeed, evidence presented in Chapter 4 suggest that Na and Cl increase in surface waters in the oil shale mining dominant regions of the Almond Catchment.

In summary, the large majority of the waste encountered at Site 4 having been heated in the former Hermand Oil Shale Works poses limited to negligible threat to the quality of the water environment in the Almond Catchment. The black unprocessed shale identified on borehole logs (appendix) and by QXRD may pose a greater risk due to the discharge of Fe and SO₄ from oxidation of limited pyrite content and discharge of elevated Cl from pore waters. Based on the investigations undertaken

here it is difficult to assess the quantity of unprocessed oil shale contained in the waste pile.

Site Conceptual Models

The observations and interpretations from the investigation works are summarised in the visual and descriptive conceptual models presented below.

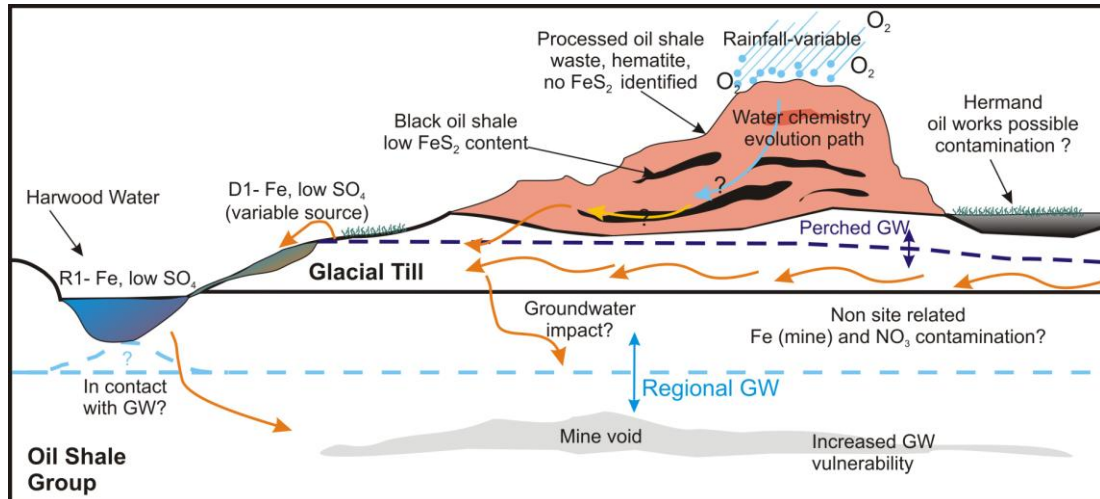


Figure 5.31 - Site 4 visual conceptual diagram indicating the principal water chemistry evolution pathway between rainfall waters and mineralised discharge waters. The variable nature of the processed and unprocessed oil shale wastes is indicated with the potential for pyrite in the unprocessed wastes. The orange arrow running beneath the pile indicates that the waters samples at the site discharge are thought to be influenced by off site water which have potentially been impacted by subsurface mines in the area. Also shown is the area associated with the former Hermand oil shale works which is likely to contain hydrocarbon contamination.

Table 5.21- Site 4 descriptive conceptual model

SOURCE		Identification		Description
		Identified	Identifier	
Pyrite		Limited	XRD	1wt% detection limit. At <1wt% in black shales, some limited visual evidence of precipitate minerals
Secondary AMD salts		No	XRD	1wt% detection limit. Possible at below detection, some limited visual evidence of precipitate minerals
Carbonates		Yes	XRD	Calcite up to 1.1wt%. Dolomite up to 3.4wt%.
Silicates		Yes	XRD	Feldspar and sheet aluminio silicates at high abundance
PATHWAY				
Discharge Chemistry	pH	6.5	Water analysis	
	Fe	2.4 mg l ⁻¹	Water analysis	Indication of limited FeS ₂ oxidation associated with black shales.
	Metals	Yes, low	Water analysis	Need to consider relative impact to receptor
Human Ingestion		Possible	Site observation	The site is partially vegetated. Evidence of excavation at the site. Public access although not prohibited is restricted.
Superficial Geology		Glacial clays	SI	Sandy clays-generally low K. However discharge cuts down into the clays Significant potential for downward water movement due to heavily mined area.
Solid Geology		Oil Shale Group	BGS Maps	Discharge waters in direct contact with solid geology. Moderate to high K, significant potential for mine void increasing groundwater vulnerability
RECEPTOR				
Surface Water		Yes- limited		Limited Fe precipitates identified on the drainage channel prior to confluence with Harwood Water.
Groundwater		Possible		Possible direction contamination to regional groundwater as discharge waters are in direct contact with solid geology.
Human Health		Possible		Limited impact on water wider environment. Possible but limited dust inhalation during summer months from site users. Also excavations suggest mine waste has been moved off site.

5.8 General discussion of mine waste

Detailed mine waste investigations are presented within this chapter at four mine waste sites; one ironstone, two coal and one oil shale. The sites were chosen to represent a cross section of mine waste found in the Almond River Catchment. Investigations documented the mineralogical difference resulting from geology, mine history and industrial history, as well as the potential environmental impact associated with the different mine waste types. Geochemistry in mine waste sites is extremely complex and the study of factors such as the movement of oxidation fronts (e.g. Evans et al. 2003), precipitate chemistry utilising SEM methods (e.g. Diehl et al. 2006) and microbial influence (e.g. Natarajan 2008) have all been successfully undertaken in recent years. This study, while indicating the influence of some of these factors, is principally focused on characterising and comparing mine wastes in the Almond with different bulk mineralogy associated with different geology and the resulting impact of mine water production and discharge.

In general the study has been successful in achieving its aims although some problems were encountered associated with XRD mineralogical identification in complex aluminium silicate mineral dominated traces and the use of chemical modelling techniques on two of the sites. One of main areas for potential improvement to the study would be to add to XRD analysis with XRF analysis and potentially SEM analysis to improve the geochemical characterisation undertaken at each site.

5.8.1 Mineralogy

The waste mineralogy from the four sites differed significantly according to the geological and historic industrial source of the waste. The bulk mineralogical assemblages at site 1, 2 and 3 were similar and consisted principally of a significant proportion of aluminium silicate minerals such as kaolinite, muscovite, illite and dickite in addition to lesser fractions of feldspars, carbonates and quartz. This is consistent with them all being mined from the Carboniferous aged Coal Measures or

the coal bearing formations of the Clackmannan Group which are dominated by mudstones, sandstone, shales, coal and occasional limestones, ironstones and seat earths (Browne et al. 1999). The principal difference between the sites is the primary pyrite content which is likely related to the depositional environment of the geological horizon from which the waste was mined. Studies on deep mines have shown that the lithostratigraphic position of coals and associated mined overburden, relative to marine bands, can influence pyrite content. In general geologies with a greater marine influence generally have higher pyrite content (Spears et al. 1999, Younger & Adams 1999, Younger 2000). For deep mines this association relationship has been used to predict mine water quality (Younger 2000). It is more difficult to directly apply this relationship to mine wastes as often the exact lithostratigraphic source of a historic mine waste is not known, however the higher pyrite content in some wastes, i.e. Site 1, suggest a more marine influenced source rock.

Jarosite content also differed at the sites, since pyrite is the source mineral for jarosite (Daoud and Karamanev 2006) this is a direct consequence of the primary pyrite content. Although jarosite was the only AGS identified by the XRD analysis, it is likely other AGS minerals, although not identified, were present in the wastes and that these may influence the site geochemistry through the storage and subsequent release of acidity (Younger 2000, 2004, Lottermoser 2010). The lack of identification of these other minerals is not surprising since many Fe precipitates have a poor crystalline structure and are often not easily identified by XRD (Younger 1995). Also, the ~1wt% detection limit of XRD analysis means pyrite and AGS minerals below 1 wt%, which could still influence the discharge water geochemistry, may not have been identified. For example other studies have shown AGS and Fe precipitate minerals such as schwertmannite and melanterite to be present at mine waste sites particularly at low pH (Espartero et al. 2005, Frau et al. 2011). Therefore, the use of other analytical detection methods, mentioned above, maybe useful in the study of mine wastes when mineralogy below 1 wt% may be of influence.

Analysis at Site 1 revealed relatively high levels of K-jarosite and pyrite, possibly suggesting a marine influence on the mined horizon from which the waste was derived. Site 2 contains discrete horizons or ‘hotspots’ of pyrite and K-jarosite, potentially indicating that some of the worked strata had a marine influence while the majority was of non-marine source. This would seem logical since Site 2 is significantly larger and was sourced from a deep, long lived mine (Oglethorpe, 2006) suggesting waste was sourced from a number of geological horizons during the progression of the mine. Site 3 contains no QXRD identifiable sulphide or sulphate mineral content suggesting a non-marine influenced source rock horizon, although, there is limited visual evidence, on waste rock surfaces, of Fe precipitate formation which is generally related to pyrite oxidation (Lottermoser 2010).

The majority of sites 1-3 contain low abundances of calcite, this is consistent with the Coal Measures geology which is generally limestone poor (Browne et al. 1999) and even the Limestone and Limestone Coal Formations (which counter-intuitively have nomenclature suggesting an abundance of limestone) are relatively limestone poor. Younger (2004) indicated that calcite cements and discrete limestone beds are extremely poor in the Westphalian Coal Measures of northwest Europe. When limestones do occur in these units they are generally dolomitic (Paul Younger 2012, personal communication). This is significant because calcite dissolution reactions rates are significantly faster than dolomite dissolution and when present calcite offers an effective acidity buffer to acidity produced by pyrite/sulphide oxidation (Banwart & Malmstrom 2001, Lottermoser, 2010). Siderite, an Fe carbonate, was identified at sites 1-3; consistent with its known abundance in the sandstones and shales of Carboniferous age coal bearing sequences (Spears 1989, Younger 2004). No ankerite, another common Fe carbonate mineral found in Scottish Coal Measures (Younger 2004), was identified; however, this is likely because the sites contain only low abundances of coal and ankerite is a late diagenetic mineral which forms primarily on coal cleat surfaces (Thomas 2002). It may have been present at <1 wt%. The silicates, such as feldspars and clay minerals, identified at all of the sites also offer some acidity buffering potential although generally at much lower reaction rates than the carbonates (Banwart & Malmstrom 2001, Lottermoser 2010).

Site 4 differs from the rest of the sites because it consists predominantly of a waste which has been significantly altered due to processing in the oil shale industry (Chapter 3). QXRD analysis revealed that processing produces a significant component of hematite in the waste as well as destroying the potential for, at least an identifiable, pyrite content. The same hematite-pyrite relationship was observed between unprocessed and processed oil shales in the Estonian oil shale industry, although in Estonian the processed oil shales came in the form of ash as the shales were burned in boilers for power generation, also the oil shales were generally more carbonate dominant than the Scottish Oil Shales (Saether et al. 2004). Mullite and cordierite were also identified, which are minerals more commonly associated with metamorphic or igneous settings and are also used in the ceramic industry (Schneider et al. 2008). Field observation and QXRD analysis indicates that the oil shale waste pile also contains a proportion of unprocessed black shale waste which contains very low levels of pyrite. Unprocessed West Lothian oil shales and those from America and Estonian have been shown to contain pyrite contents up to 5wt% (Louw & Addison 1985, Saether et al. 2004). The calcite and dolomite contents identified in the waste at up to 1-3 wt% are slightly higher than those identified in the unprocessed oil shales by Louw & Addison (1985); this, however, could be a consequence of improved analytical equipment and techniques. Also there is a loss of mass between the unprocessed and processed waste which could explain the difference.

5.8.2 Hydrogeochemistry

An inverse PHREEQC model was used to investigate and quantify the dominant geochemical reactions accounting for the mine water evolution at each of the sites. Although some difficulties were encountered with the models; using the known mineralogy of the waste produced solutions which give a robust representation of the dominant geochemistry at the sites. This approach could be said to be an improvement on the application of similar approaches in the Almond Catchment to mine water where only the assumed mineralogy was used as a model input (e.g. Chen et al. 1999). The models suggested that mine water evolution in mine wastes

which discharged significant concentrations of Fe and SO₄ can be explained principally by pyrite oxidation and K-jarosite dissolution. This relationship has been recognised for similar mine wastes in the UK (e.g. Costigan et al. 1981, Banks et al. 1997) and around the world (e.g. Banwart & Malmstrom 2001, Espanna et al 2005, Nordstrom 2009, Lottermoser 2010).

The model solutions also suggested that coincidental buffering of proton acidity at these sites is likely to be related to carbonate and dolomite buffering in addition to a component of silicate buffering. However, as mentioned above calcite is generally lacking in the Scottish Coal Measures and although some low abundance were identified it is possible that siderite and possibly ankerite dissolution played a greater role than suggested by the model solutions (Younger 2004). Ca and Mg concentrations in discharge waters were resolved by the models via calcite and dolomite dissolution; however at Site 3 no dolomite was identified despite the fact that the discharge water contained Mg. If ankerite, Ca(Mg, Fe)(CO₃)₂, was present this could account for the source of the Mg, one possible explanation is that ankerite was present at below 1wt%. In general the Al content increases are explained by the model solutions through aluminium silicate buffering of proton acidity, indicating the importance of aluminium silicates as sources of Al in discharge waters (Younger & Sapsford 2004, Lottermoser 2010).

At Site 1, the ironstone waste, the model solutions suggested that carbonate buffering, while significant, maintains only low pH values, a clear indication that acid generation dominates acidity buffering, and it is suggested that in future this buffering capacity could be exhausted prior to the acidic production (e.g. Banwart & Malmstrom 2001). If this occurred it is likely to result in an increase in dissolved contaminant concentrations. Banwart & Malmstrom (2001) present a preliminary assessment method to predict when this loss of carbonate buffering would occur at a mine site, however because of the already very low calcite and dolomite content and the potential complexity in the role siderite, aluminium silicates and possibly even ankerite (though it was not identified) application here is not considered appropriate. Indeed the Banwart & Malmstrom (2001) largely ignores the role of siderite or

ankerite which is thought to significant influence mine water geochemistry (Younger 2004).

At the former Whitrigg colliery, Site 2, the models suggest that carbonate buffering dominates and maintains near neutral pH but this influence is primarily related to the ALD trench installed at the site and not the general buffering capacity of the waste pile. This is consistent with the design of the trench (PIRAMID 2003) but as a result the model only partially explains the geochemistry of waste pile. To truly gain a more accurate assessment of the site geochemistry an inverse model would need to be applied the waters sampled prior to entering the ALD. As with Site 1 it is possible that siderite or ankerite played a role in the site geochemistry (Younger 2004) but that this was not revealed by the model solutions. The model solutions are inherently non unique (Parkhurst & Appelo 1999) and because ankerite was not identified by XRD its potential role was not modelled. The model solutions from Site 3 and 4 also suggest carbonate and silicate buffering reactions are involved in the evolution of waters. At Site 3 no pyrite was identified by the XRD analysis, however its inclusion was necessary to balance the SO_4^{2-} and Fe in discharge waters. The site was also further complicated by the peat bog area through which the discharge waters moved.

At Site 4 the same pyrite, carbonate, aluminosilicate reactions as mentioned above are occurring, however, the scenario is complicated by there being in effect two different wastes (processed and unprocessed oil shale) and mineralogical assemblages. Pyrite, known to be present in the unprocessed oil shale (Louw & Addison 1985), was used in the model to balance the Fe and SO_4^{2-} in discharge waters. Some of the model solutions suggest that hematite might be involved as a source for Fe. This is considered unlikely since an excess of acidity would be required to mobilise Fe from hematite (Faust & Aly 1981).

Model solutions for sites 1 and 2, which were produced with low uncertainty values, are considered feasible based on the mineralogy of the waste, although as mentioned above may overlook the involvement of some Fe carbonates and AGS minerals not identified by the XRD analysis. The solutions agree with many of the other principal

mine water evolution relationships documented in other mine waste studies, namely 1) pyrite oxidation being the main source of contamination, 2) AGS formation and dissolution reactions delaying direct acidity release from pyrite, 3) goethite precipitation providing a sink for Fe, and 4) carbonate and silicate dissolution reactions buffer acidity but co-incidentally release major ions and also some metals into discharge waters (e.g. Costigan et al. 1981, Banks et al. 1997, Banwart & Malmstrom 2001). Site 3 and 4 only returned solutions when uncertainty values were increased to levels not considered to be acceptable in offering definitive representation of the site hydrogeochemistry. At Site 3 this is possibly related to the discharge samples being recovered some distance away from the mine waste once the water has moved through a vegetated peat area where complex organic chemistry may have altered the mine waste chemical signature probably by the immobilisation of dissolved metals through sulphate reduction (Hedin et al. 1994, Younger 1995, PIRAMID 2003). Another explanation is that minerals not present in the recovered samples or with abundances less than 1wt%, and not identified by the XRD, exert much of the control over the discharge geochemistry. At Site 4, geology and hydrogeology indicates that the waste pile may only be of partial influence on the sampled discharge water which is likely to incorporate field drainage and possibly inputs from mine sites. Therefore the use of the site mineralogy in isolation to resolve the sampled discharge water source proved problematic.

These results emphasise the importance of accurate and robust design of site investigations when assessing environmental problems associated with mine waste. It is considered that while the investigations here identified the main site geochemistry, some of the complexities of the system were overlooked. For example XRF analysis may have been useful to more accurately constrain site geochemistry below the 1wt% detection limit of XRD analysis.

5.8.3 Environmental impact

Varying degrees of potential environmental impact were observed associated with each of the sites. Site 1, the ironstone waste, is considered to have the greatest potential to impact the surface water and groundwater environment due to high Fe

(up to 160mg l^{-1}), Mn, Al and SO_4 (up to 800mg l^{-1}) concentrations and low pH (2-4) in discharge waters which have produced significant volumes of Fe precipitates along the length of its discharge stream. The formation of Fe precipitates has been shown to significantly impact river ecology (Edwards and Maidens, 1995) and aluminium is known to be highly damaging to surface water environments (Younger & Sapsford 2004) because of its eco-toxic nature. However, once the discharge waters are mixed with less acidic riverine waters this is likely to cause Al precipitation as an aluminium hydroxide reducing mobility in the surface environment (Younger and Sapsford 2004). Drinking waters in West Lothian are generally not sourced from private water supplies; however, mine waters have been shown to impact water supplies elsewhere in the world (e.g. Bird et al. 2009).

Site 2 also has a significant potential to impact the surface and groundwater environment due to the high Fe ($\sim 80\text{mg l}^{-1}$), Mn and SO_4 (680 mg l^{-1}). The installed treatment system at the site reduces the potential impact of direct discharge to surface water. However, waters sampled even before the main influence of the treatment system show lower concentrations of Fe than those at Site 1. After the influence of the treatment system there is evidence of the adverse impact of the site on the local watercourse in form of Fe precipitates, as with Site 1 this is likely to result in impacts on river ecology (Edwards and Maidens, 1995). One potential significant difference between the two sites is the mine shaft known to be directly below the Site 2. This may offer a direct route for the migration of contaminated waters from the site to the regional groundwater body. Secondary impact from the site may result from smaller diffuse discharges around the edges of the waste.

Site 3 shows some limited evidence of Fe precipitate formation and lower Fe ($\sim 1\text{mg/L}$) concentrations. The impact of this on associate surface water ecology is likely to be limited. As with Site 2 there is a historic mine shaft within meters of the mine waste which may offer a direct route for groundwater contamination.

Site 4 appears to have little impact on the surface water environment due to similar background Fe concentrations already found in Harwood water, however, the

elevated Mn concentrations in water may be of some impact. While this site in isolation may not have a significant impact on the water environment, the investigations suggest that oil shale waste do discharge metals. The diffuse impact of contamination from oil shale wastes in the catchment is likely to be a contributor to Fe loading in the Almond River. Oil shale waste elsewhere in Europe is known to discharge acidic, metal rich leachates as well as hydrocarbon and phenol contaminants (Seather et al. 2004)

The discharge of Fe from each of the sites and other mine wastes and deep mines within the Almond and across the mined areas of Scotland (and the UK) are the principal cause of poor groundwater classification under the WFD classification requirements (SEPA 2007).

The relationship between environmental impact, mine waste source and mineralogy identified within this study offers potential insight in the impacts associated with mine waste in the Almond Catchment and elsewhere. This study suggests that mine wastes derived from horizons containing iron stones, with high pyrite contents, potentially due to a stratigraphic association with marine deposition, are of greatest environmental concern due to the discharge of highly acidic, metal rich waters. While this study only represents a snap shot of 4 sites in the catchment with one of those sites showing ironstone with elevated pyrite content, evidence from other studies supports this. For example, Heal & Salt (1999) investigate ironstone bearing mine waste, close to Site 1 within the Almond Catchment, which also discharges waters with low pH (~2.6) and high metal and sulphate concentrations (~50 mg/L Fe, 20 mg/L Mn and 1700mg/L SO_4^{2-}), Wiggering (1993) describes Upper Carboniferous aged mine waste spoils from Germany with pyrite content and siderite concretions which in the long term discharge acid leachates (~pH- 3) rich in heavy metals, and Younger (2002) describes the very acidic, metal rich (pH- 3.3, Fe up to 1220 mg/L) discharges from flooded mines and spoil heaps in siderite iron ore fields in Cleveland UK.

The coal mine wastes, Sites 2-3, studied in the catchment show generally lower bulk pyrite content. Localised hotspot horizons or zones of pyrite and jarosite are identified in Site 2 and no pyrite content is identified at Site 3 suggesting negligible pyrite content or pyrite below the 1wt% XRD detection limit. Site 2 discharges waters (Fe up to 80 mg/L) similar to many of the documented coal spoil wastes derived from similar Carboniferous aged geology (e.g. Younger 2001, Rees et al 2002). Site 3 discharge waters have much lower iron concentrations due to limited or only partial influence of pyrite oxidation, similar low Fe coal mine spoil waste discharges been identified in Banks et al (1997). This suggests that coal spoils derived from Carboniferous Coal Measures in the Almond and elsewhere can not be typified by one type of discharge chemistry.

The oil shale mine waste investigated is only a small site compared to the vast oil shale bings around West Calder and Broxburn. The waters discharged to the environment, either surface or groundwater, are likely to be similar to the Hermand Oil Shale water because waste mineralogy will be controlled by similar industrial processing. However, the most significant feature identified at Site 4 is the presence of unprocessed black oil shale waste incorporated with the red orange processed shales. It is these black oil shales or blaes which are most likely responsible for the slightly elevated Fe concentrations in the discharge waters. Oil shale wastes elsewhere have been shown to be of environmental concern (Saether et al 2004). The kukersite oil shales in Estonian are carbonate rich shales and therefore have significant buffering capacity, however, the dictyonema Oil shales in Estonian, which are mineralogically similar to the West Lothian Oil shales, have been shown to generate acidic leachate due to pyrite oxidation (Puura & Pihlak 1998). One explanation why no significant acidic discharges have been documented in the Almond associated with the massive oil shale wastes is because the unprocessed wastes were deposited together with the processed wastes. The processed wastes contain no acid generating minerals and 1-2 wt% calcite, therefore it is possible the calcite in the processed wastes buffers acidity generated from the unprocessed waste in the pile. This mixing of the waste streams if applied to the Estonian industry, which still operates today, could be one possible solution to limit the environmental

impact of the oil shale waste. However although no significant acidic discharges are observed in the catchment the unprocessed oil shales together with weathering of the processed oil shale may result in oil shale waste being a significant diffuse source of mine related contaminants in the Almond Catchment.

5.8.4 Summary of Mine Wastes

Outlined in Table 5.22 is a summary of the main features associated with the investigation into mine waste in the Almond River Catchment.

Site		Polkemmet Moor Ironstone	Whitrigg Colliery	East Benhar	Hermand Oil Shale
Origin		Ironstone band in the Scottish Coal Measures	Passage Group, Upper Limestone Formation and Limestone Coal Formation	Sandstone and mudstone lithologies in the Scottish Coal Measures	Oil Shale from the Scottish Oil Shale Formation. Processed at the Hermand site.
Mineralogy		Clay minerals, pyrite, jarosite, goethite with some feldspars and carbonates	Clay minerals, quartz, feldspars and limited pyrite, carbonates, jarosite and goethite	Clay minerals, quartz, feldspars, carbonates, some siderite and goethite	Quartz, hematite, sheet aluminium silicates, carbonates, corderite and mullite. Pyrite in black oil shales
Dominant Geochemistry		Pyrite oxidation and jarosite dissolution with partial pH buffering from carbonate and silicate dissolution	Pyrite oxidation and jarosite dissolution balanced by dominant carbonate buffering, limited silicate dissolution reactions	Limited dissolution (weathering) of carbonates and silicates. Limited pyrite oxidation.	Limited dissolution (weathering) of silicates, carbonates and possibly pyrite in low abundance. Possibly hematite dissolution.
Mine water Chemistry	pH	2-4	6	6-7	6-7
	SO₄²⁻	Up to 800 mg l ⁻¹	Up to 670 mg l ⁻¹	Up to 20 mg l ⁻¹	Up to 25 mg l ⁻¹
	Fe	Up to 160 mg l ⁻¹	Up to 80 mg l ⁻¹	~1mg l ⁻¹	Up to 2.4 mg l ⁻¹
Environmental Impact	Classification	Acidic, SO ₄ dominant	Slightly acidic, SO ₄ dominant	Alkaline, SO ₄ moderate	Alkaline, SO ₄ moderate
	Potential	Significant Fe precipitate and jarosite formation for over 1km of stream bed prior to discharge to Almond River. Likely to be a significant contributor to Fe in Almond river waters.	Reduced impact due to treatment system. However, Fe precipitate formation is still prominent along local water course (Latchburn). Likely to contribute to Fe in Almond river waters.	Limited environmental impact potential. Some evidence of Fe precipitate formation, limited diffuse contributor to Fe in the Almond water environment.	Some evidence of Fe precipitate formation, diffuse contributor to Fe in the Almond water environment. Observed impact on local surface water is negligible
Notes		Potential for future worsening of discharge chemistry if carbonates are exhausted prior to acid producing minerals.	Without treatment system significant impact on local water quality. Possibility of direct impacts to groundwater due to abandoned mine shaft.	Peat and reed vegetation may be offering natural 'treatment' of site waters.	Some evidence of pyrite content in black oil shale waste. Overall volume of black shale waste in the catchment maybe significant as a contaminant source.

Table 5.22 - Comparative summary of the main mine waste features from the four sites investigated in this chapter.

5.8.5 Mine waste and catchment geology

There are almost 100 different mines waste sites in the catchment. The mineralogy and mining history from the representative mine sites investigated within this chapter together the regional geology give an indication of the potential prevalence of each of the different mine wastes types (Figure 5.32).

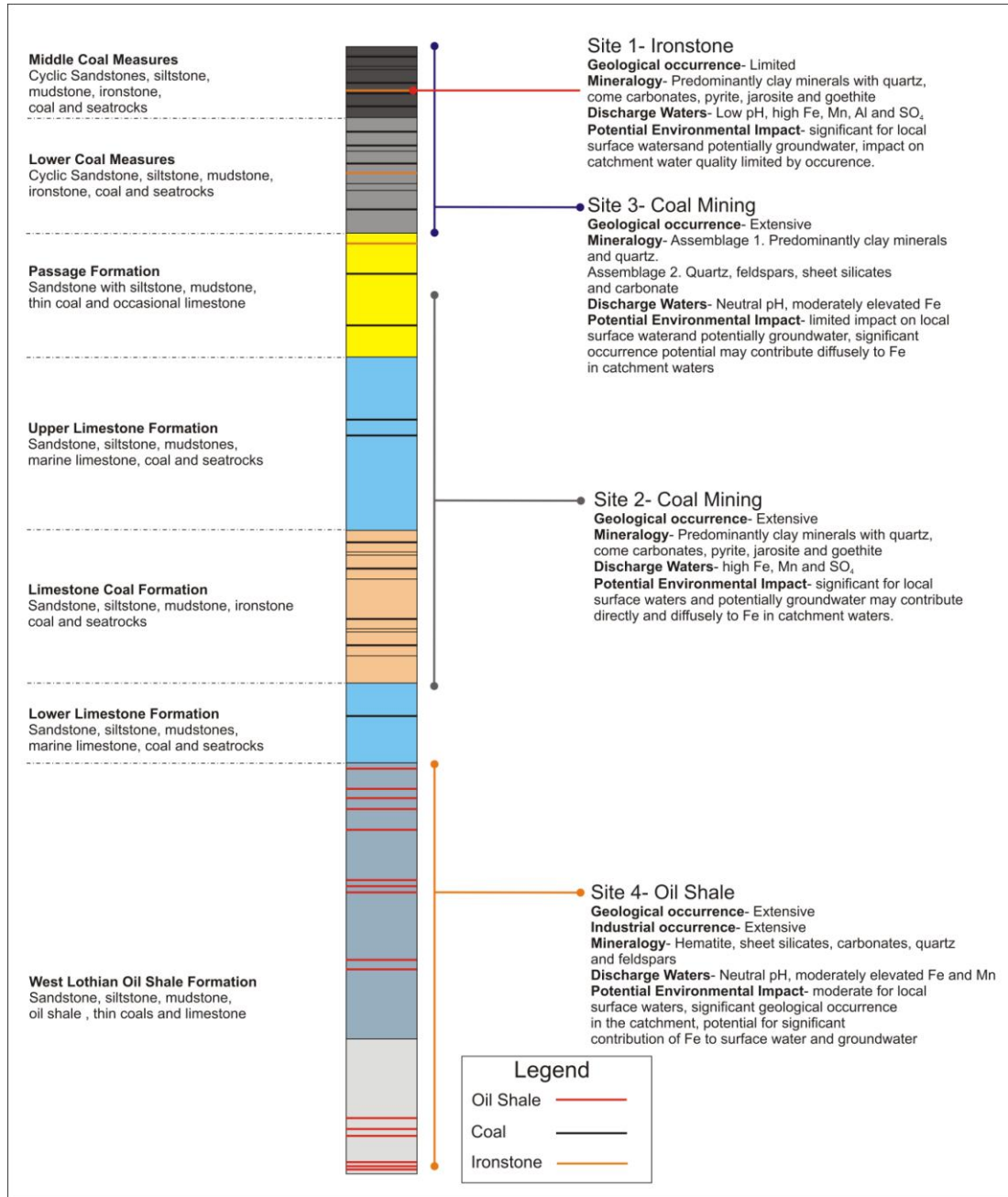


Figure 5.32 - Representative Generalised Vertical Section of the Almond Catchment sedimentary geology and the association of mine waste.

Ironstone bands occur only occasionally in the geological succession of the Almond Catchment featuring in only a number of places; named examples include the Crofthead Slaty Band Ironstone and the Upper and Lower Denny Blackband Ironstone (MacGregor et al 1923). This indicates that while ironstone wastes discharge significantly contaminated waters, due to high pyrite content, the potential prevalence of ironstone waste and cumulative influence on catchment water quality is limited compared to other mined rocks. This is potentially true not only for Almond Catchment but for the majority of mined areas as although ironstones are formed from common products of weathering they are considered a subordinate sedimentary facies (Van Houten & Bhattacharyya 1982) and bands occur much less commonly than coals (MacGregor et al. 1923). Also, in general working for ironstones from the Westphalian Coal Measures was by hand which produced only small amounts of waste compared to more mechanised and long lived coal or oil shale mining (Palumbo-Roe et al. 2010). In contrast working of Jurassic aged ironstones from areas such as Northamptonshire, North Yorkshire and Cleveland produced significant quantities of ironstones waste, only some of which has been cleared and restored (Palumbo-Roe et al. 2010)

Oil shale is the foremost waste, at least in terms of volume and visual impact, in the catchment due abundant geological occurrence in the West Lothian Oil Shale group (Cameron & Stephenson 1985) and the historic size of the oil shale industry (Hallett et al. 1985, Kerr 1994, Harvie 2004). This has resulted in a large quantity of oil shale waste, up to ~150million tonnes (Harvie 2004, 2005). In general, the majority of this waste, having been processed, poses little potential impact to water quality in the catchment; however, it is difficult to be certain of exactly how much unprocessed oil shale is present at the larger oil shale sites in the catchment. This differs significantly from the Estonian oil shale industry where large quantities of unprocessed oil shale mine waste discharge acidic waters (Saether et al. 2004). If Fe and Mn concentrations at large sites in the Almond are similar to those sampled at Site 4 then this represents a large potential source of diffuse contaminant. Furthermore, while the processed orange red oil shale has limited influence on discharge chemistry it is not totally inert and may influence water quality, particularly due to carbonate and

aluminium silicate weathering, which can increase dissolved metal concentrations and increase electrical conductivity values (Lottermoser 2010).

The West Lothian Oil Shale group is limited in extent to the Almond catchment, the area to the north around Linlithgow and 2 small areas in Fife and East Lothian (Francis 1983, Brown et al. 1999). Therefore while oil shale waste is important in the Almond it is unlikely to represent a significant environmental treat elsewhere in Scotland and UK. Globally however, there are still huge quantities of oil shale to be exploited and similar water quality issues to those seen in Scotland and Estonia may arise from current and future exploitation of oil shale (Brendow 2003).

Coals are common throughout the Carboniferous aged geology of the catchment featuring in every major geological formation and with greatest frequency in the Limestone Coal Formation and Scottish Coal Measures (Cameron & Stephenson, 1985, Browne et al. 1999). The depths of mines associated with Site 2 and 3 were compared to BGS geology series maps and cross sections (BGS solid/bedrock maps- Livingston 32W and Falkirk 31E) to give an estimate of the geological horizons from which the waste may have been derived; this is shown on Figure 5.32. It can be seen for these mines and potentially many others in the catchment that coal mine wastes are derived from a huge variety of different lithologies. This presents a problem when associating potential environmental impacts with coal mine wastes. Pollution potential can not be estimated based solely on the fact that waste originated in a coal mine, as can be seen by the difference in the composition of discharge waters between Site 2 and 3. Some overburden from coal mines may contain only sandstone or limestone with no pyrite; while other overburden may contain mudstone formed in marine influenced anoxic depositional environments with significant pyrite content (Spears et al. 1999, Younger & Adams 1999). Both of these are considered as coal mine waste but are likely to represent a different potential environmental treat. This is a problem, particularly for the regulator or planning officer not familiar with coal measure geology or mine waste. This is exacerbated by literature on coal wastes which generally only feature those coal mine waste sites which represent a significant environmental concern. Of course, this is the reason why these particular

sites feature in the literature but to a person unfamiliar with mine waste mineralogy and lithology it can lead to the impression that all coal mine wastes discharge acidic, low pH waters as defined in Rees et al (2002).

It is beyond the scope of this study but classification of coal mine waste types based on dominant lithology might be useful as a screening tool to eliminate those mine wastes which are unlikely to be of environmental concern. It may even be possible to use mine waste colour from aerial maps or remote sensing as a screening tool for mine waste discharge impact potential.

5.8.6 Treatment Potential

It was not the intention of this investigation to argue for the need for mine water treatment at any of the sites investigated. Ultimately, this is a task for environmental regulators and local authorities. Having investigated the range of mine waste sites in the catchment, however, it seems prudent to explore the potential remediation options for each. Particularly for Site 1 which has significant environmental impact on surface water and appears almost as an oversight in environmental management, when compared to the much lower contaminant concentrations recorded at Site 2, where a treatment system has been constructed.

The discharge chemistries associated with the mine waste sites in the Almond Catchment present a number of challenges associated with potential treatment options. Minimisation of the impact on local and catchment water quality will require, dependent upon the discharge chemistry and source; pH increase, alkalinity increase, reduction in metal concentrations Fe, Mn, Al, and SO₄ concentration reduction. In Chapter 2 the main types of treatment used for mine waters are discussed. This discussion was used to inform the potential treatment options for waste in the Almond Catchment. Outlined in Table 5.23 below is a summary of the options based upon the representative study in this chapter.

Mine Waste	Key Treatment Requirement	Potential Treatment Option
Ironstone	Increase pH, decrease Fe, Mn, Al and SO ₄	Anaerobic Wetland Treatment, Anoxic Limestone Drains
Coal	Decrease Fe, Mn and SO ₄	Aerobic/Anaerobic Wetland Treatment
Oil Shale	Decrease Fe, Mn	Aerobic Wetland Treatment

Table 5.23- Mine waste types investigated in the Almond and potential treatment options

5.9 Chapter Conclusions

- Site investigations at the four chosen sites revealed that mine waste in the Almond Catchment show significant mineralogical variability dependent upon mine waste source and industrial history.
- The inverse model function in the modelling code PHREEQC was used, with varying levels of success, to better explain the evolutionary history of waters discharged from sites.
- Mine water discharge chemistry associated with different mine waste sites showed variability in Fe, SO₄, pH and heavy metal concentrations shown, using an inverse model, to be principally associated with pyrite and jarosite contents. However, it is considered that siderite and ankerite dissolution may play a role.
- Carbonate and silicate buffering was, shown in model solutions, to maintain discharge pH at differing values dependent upon mineralogical abundance. Aluminium silicate buffering was interpreted as the principle source of aluminium in discharge waters.
- The potential environmental impact associated with different sites varied, the ironstone mine waste, Site 1, was shown to have the highest potential environmental impact while the coal, Site 3, and oil shale mine waste, Site 4, was shown to have the lowest. The coal wastes showed differing environmental impacts, even with the installation of a mine water treatment system at Site 2, related to differing pyrite and jarosite content.
- The orange red processed oil shale waste, which dominates the bulk of the waste at Site 4, contained no identifiable pyrite or sulphate mineral content but up to 15wt% hematite, a feature thought to be related to the wastes industrial processing history. Discrete layers of black unprocessed shales were identified at the site and XRD analysis suggest they may contain limited pyrite content.
- Evidence suggests that settlement pond sediments associated with the historic colliery at Site 2 may contain significant pyrite and jarosite contents which

are the main source of acidity associated with the sites discharge water evolution.

- Several of the sites were found to be in close proximity to, or even overlay, historic mine shafts or mine void; these were highlighted as potential pathways for the movement of contaminated water to regional groundwater bodies.
- The large volumes of Fe precipitate on discharge streams associated with Site 1 and 2 were interpreted as potential sources of increased Fe concentrations in catchment waters under high flow conditions (as documented in Chapter 4).
- Relating the mine waste mineralogy and mine site history to the catchment geology indicates that ironstone mine wastes are unlikely to be abundant in the catchment compared to coal and oil shale wastes.
- A range of different treatment technologies would need to be used to treat the mine waters sampled.

Chapter 6

Mapping mine water hazard

6.0 Chapter summary

In this chapter mine water chemistry and hazard is characterised with the presentation of data from a mine water sampling investigation in the Almond River Catchment. Several mine site hazard categories are defined based on the chemical composition of the sampled mine waters using different water chemistry classification schemes. Ironstone mine waste discharge waters are identified as the most hazardous followed in order of hazard by Flooded Coal Mine, Coal Mine Waste, Flooded Oil Shale and Oil Shale Waste. The results of geochemical modelling and site characterisations presented in Chapter 5 supported by mine site characterisations presented in other studies indicates that mine site lithology and mineralogy is the principal control on discharge chemistry. Additionally mine abandonment age and the reduced availability of oxygen are of secondary influence on the water quality of flooded oil shale mines.

Hazard characterisation is utilised to construct the first mine water hazard map for any heavily mined region. The catchment is divided into sub-catchment areas and four hazard classes are assigned, A-Limited, B-Significant, C-Important and D-Extensive, based on the frequency and type of mine site within each sub-catchment area. The potential use of the map is discussed in the context of current catchment management and the water quality improvement targets outlined by SEPA in accordance with the European Union Water Framework Directive.

6.1 Introduction

The Almond Catchment, having been heavily mined for an extended period, using a number of methods, in a range of lithologies, represents a complex geochemical environment for the production of mine waters. Principal factors which influence mine water evolution include

- mine site mineralogy (Chapter 5)
- hydrogeology and mine site morphology (Rees et al 2002),
- mine abandonment age (Younger 1997),
- coal seam sulphur content (Younger & Adams 1999)
- stratigraphic relationships (Younger 2001) and
- mine water stratification (Nuttal & Younger 2004) .

These factors are likely to operate to varying degrees at the range of mine site types present within the Almond Catchment, which include:

- coal mines with a range of abandonment ages (25-200+ years)
- coal mine wastes with variable mineralogy
- ironstone mine waste (with high pyrite content)
- oil shale mines with a range of abandonment ages (50-160 years)
- spent oil shale waste with a depleted pyrite content together with overburden or inferior oil shale mine waste

Mine water chemistry and particularly dissolved metal content is the principal cause of hazard associated with mine water discharge. There has been considerable work undertaken on the characterisation of mine water chemistry (Glover 1975, Hedin et al 1994, Younger 1995, Rees et al 2002) and mine water hazard assessment (Gray 1996, Kuma et al 2011). Maps of environmental hazard are commonly used in the field of geoscience: examples include landslide hazard maps (Guzzetti et al 2000), flood risk maps (Büchele et al 2006), seismic hazard maps (Slejko et al 1998) and coal mine subsidence maps (Oh & Lee 2011). However, at present there are no notable examples of hazard maps being used to represent mine water hazard.

National scale maps of groundwater vulnerability underpin the regulatory approach to groundwater protection in the UK. When the latest Scottish groundwater vulnerability map was released one of the potential applications of the map was that it be used in conjunction with land use and hazard maps (Ó Dochartaigh et al 2005). As abandoned mines are one of the principal threats to both surface water and groundwater in Scotland (MacDonald et al. 2005) and the rest of the UK a mine water hazard map is considered to be a powerful tool for sustainable water management, particularly when used in conjunction with vulnerability maps and other environmental assessment methods. In this chapter mine water chemistry and hazard is characterised using sampled mine water recovered during extensive reconnaissance and sampling fieldwork. Mine water hazard is then mapped using mine site hazard and frequency within sub catchment areas defined by an accurate digital terrain model. The catchment hazard map will help to prioritise actions, direct further investigation, improve monitoring and potentially assist in the targeting of remediation. This is particularly relevant in the context of ambitious environmental improvement targets required by the EU Water Framework Directive.

6.2 Site selection

Characterisation of mine water chemistry in the catchment required the recovery of representative samples from flooded mines and mine wastes, with a reasonable geographic spread, in both the coal and oil shale dominant mine areas. Identifying and sampling appropriate sites was done through a number of investigation methods outlined below;

- GIS- the mine site data set and maps presented in Chapter 4 were used to select a number of areas of high mine density in the coal and oil shale dominant mining areas.
- Reconnaissance and Sampling Fieldwork- several weeks exploring heavily mined areas in the catchment to identify, document and sample mine waters.
- Coal Authority- provided a list of known discharges in the catchment together with some limited chemistry data.
- Historic information sources- mine plans available from BGS archives in Edinburgh (Figure 6.1) were used to identify potential mine water discharges.

The plans were of most help in identifying oil shale discharges as this type of discharge proved difficult to identify on the ground. The difficulty was principally due to the oil shale dominant area being significantly more urbanised than the coal dominant area.

- Data from external sources including BGS data, Coal Authority (CA) data and data presented in literature.

Nineteen mine water samples were recovered from sixteen sites in the field. Data for seven mine water samples in the catchment sampled by either the BGS, the CA or as part of investigations outlined in literature has also been used, the source of the data is outlined in Table 6.1. In total 26 mine waters in the catchment are used to characterise mine site hazard.

All the sites contained on the CA list were visited, however, only half of the sites could be identified on the ground and sampled, these are: Levensseat, Le, Whitrigg, S2, Cuthill 1, Cu1, Cuthill 2, Cu2, Stoneyburn, Sb and Polbeth, Po. (Cuthill 1 was visited but could not be accessed due to the mine water remediation scheme in operation at the site; data was sourced from Younger (2001) see Table 6.1 below). A sample was recovered at the national grid reference given for a discharge in the oil shale area, 'Laws Pit' however the returned chemistry of the sample suggested it was field drainage and not mine water origin; therefore, it has not been included. Twelve of the samples were recovered from previously un-identified mine waters, these being Polkemmet Moor Ironstone, S1, East Benhar, S3, Moss, Mo, Fauldhouse, Fh, Moss Hall Farm, Mh, Stoneyburn, Sb, Seafield, Sf, Hermand, S4, Woodmuir, Wd, West Calder 1, Wc1, West Calder 2, Wc2 and Ingliston, In.

Mine Water	Abb.	Study	Comments
West Benhar	WB	Salt et al, 2001; Benhar Bing Reclamation Report	Data of site drainage chemistry sampled prior to reclamation and wet land treatment project
Cuthill 1	Cu1	Younger, 2001; Mine Water Pollution In Scotland...	Data from table 1 'Representative chemical analyses of selected Scottish mine waters'
Polkemmet	Pk1	Chen et al, 1999; Modelling mine water evolution at Polkemmet Colliery...	Data from table 1 of chemical analysis of mine waters in mine shaft
Riddochhill	Ri	Chen et al, 1999; Modelling mine water evolution at Polkemmet Colliery	Data from table 1 of chemical analysis of mine waters in mine shaft
Polkemmet	Pk2	BGS Baseline study	Water sampled from Polkemmet adit by the BGS using the same sampling and analysis method outlined in Chapter 5
Millers Bridge	Mb	Coal Authority supplied data	Limited data from historic database
East Handax Wood	Hw	Coal Authority supplied data	Limited data from historic database

Table 6.1 - Mine waters in the Almond Catchment from previous studies (*The data available for these mine waters is limited compared to the sites sampled on the ground; however, they are included as they make a significant contribution to the understanding of mine water hazard in the catchment.*)

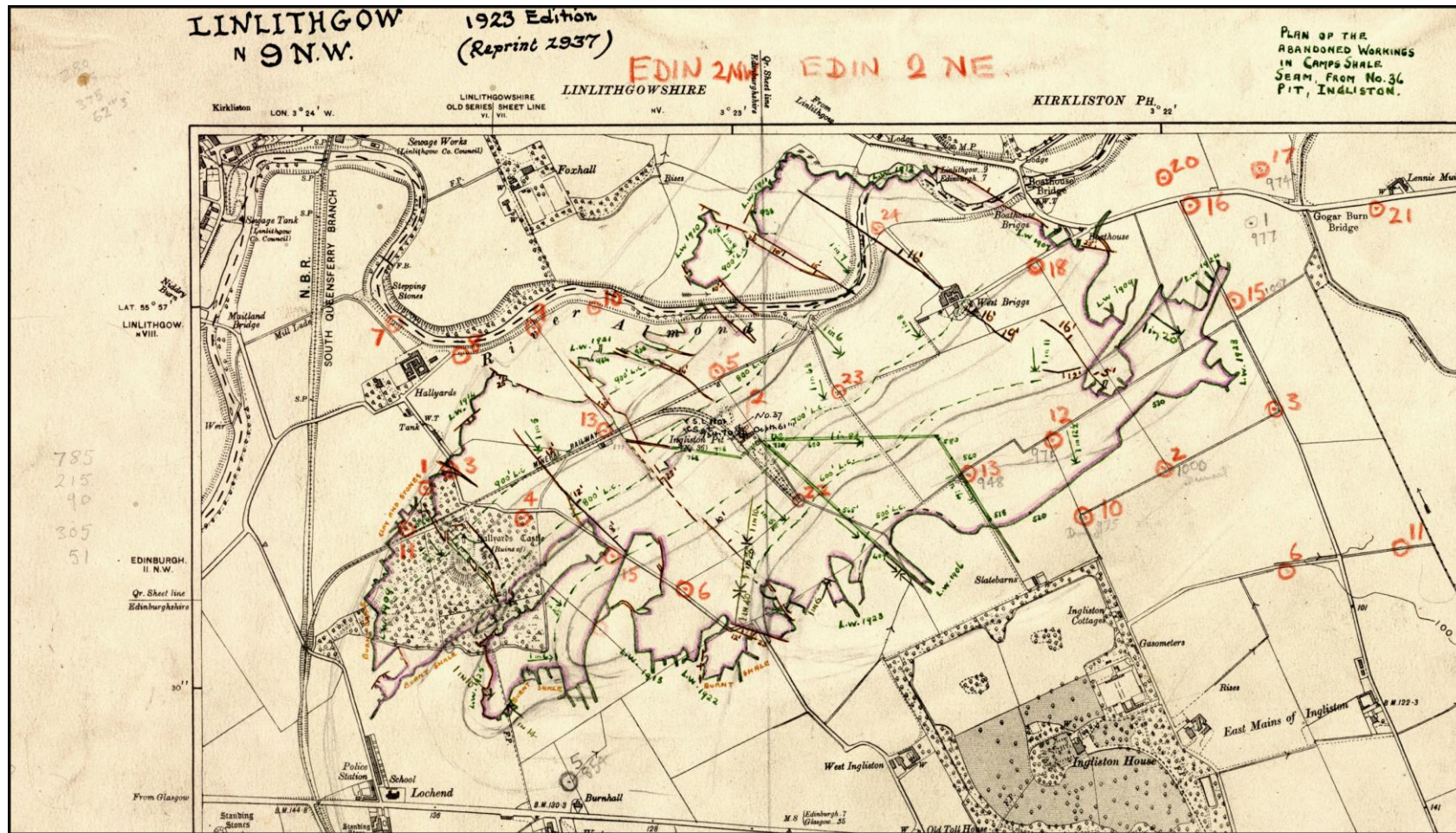


Figure 6.1- Example of a historic mine plan used to identify probable location of an oil shale mine water discharge (Ingliston, the area south of the river is now occupied by the runway at Edinburgh airport) in the Almond Catchment. The purple lined edge shows the extent of historic subsurface mining.

6.3 Sampling

Mine waters sampled in the field were analysed on site for pH, Eh, conductivity and temperature using either a Hach or Mettler Toledo portable probes which were calibrated daily and checked regularly, particularly when moving between different water types. No issue with drift or inaccuracy in meter readings was observed. Bicarbonate alkalinity, as CaCO_3 , was also recorded at the time of sampling using a portable titration kit. Titrations were made in triplicate ensure precision and average readings calculated. Bicarbonate alkalinity as HCO_3^- was calculated by multiplying the averaged reading by 1.22. Samples of the water, filtered using $0.45\mu\text{m}$ disposable filters, were collected in 30 or 60ml nalgene plastic analysis bottles and acidified to 1% v/v with Aristar HNO_3 on site.. The samples were placed in refrigeration and sent to the BGS labs in Keyworth for analysis of major ions and trace elements.

Historically iron (Fe) in mine waters was often determined from an unfiltered sample, not from a filtered sample as described above. Therefore the Fe data for flooded coal samples, Cu1, Pk1, Ri, Hw and flooded oil shale mine sample Mb, coming from historic investigations, will generally be $\text{Fe}_{\text{Unfiltered}}$. Rees et al. (2002) demonstrated that UK mine waters generally have total $\text{Fe}_{\text{Filtered}}$ values that account for over 80% of total $\text{Fe}_{\text{Unfiltered}}$ content. This may positively skew these samples compared to the sites sampled as part of the field investigations in this study where $\text{Fe}_{\text{Filtered}}$ was analysed and is presented. Pk1 and WB Fe data is $\text{Fe}_{\text{Filtered}}$. This potential skew is unfortunate but is an issue inherent in using historic and variably sourced data. The impact on mine water characterisation which uses a number of chemical parameters, in addition to Fe, is considered to be acceptable.

Considerable time, thought and discussion (with Christopher McDermott (University of Edinburgh), Alan MacDonald (BGS) and Neil Brown (West Lothian Council)) was given to scheduling oil shale waste mine water discharges for total petroleum hydrocarbon (TPH) analysis to identify any potential hydrocarbon contamination associated with residual oil which maybe able to leach from partially processed oil

shale waste. A decision was made against this primarily because investigations (Chapter 3) revealed that the application of considerable heat (+500°C) was required to remove oil from oil shale in the Shale Oil Industry. This heat transforms the organic content of the shale into oil; there is no free moving oil within the oil shale matrix. Therefore to leach hydrocarbons from oil shale in a waste site would also require considerable heat this is considered to be extremely unlikely in the natural environment.

Detailed analysis of historic documents, following the scheduling of samples, revealed that it was common place to use oil shale waste material as a filter for hydrocarbon contaminated waste waters at processing sites (Chapter 3). Also continued burning of oil shale waste on the waste pile was common, although only in the early years of the industry, potentially this may have mobilised hydrocarbons. This maybe an area where further work is undertaken in future, however, the quantity of oil shale waste contaminated in this way compared to the total volume in the 'bings' is likely to be small and the environmental impact difficult to quantify.

Every oil shale waste in the catchment was visited during fieldwork except the Tarbrax waste site, close to Cobbinshaw reservoir in the south of the Almond Catchment. The free draining nature and size of the oil shale waste sites made identifying mine water discharge streams extremely difficult. Often small stagnant surface water pools were found around the edges of oil shale waste; however, these areas were generally also occupied by cattle or arable farming so no samples were recovered. Samples were only recovered where a definite discharge could be identified i.e. at Polbeth, Seafield, Hermand.

Due to difficulty in obtaining mine water discharges at oil shale waste sites a simple leachate analysis, using 50g of sieved waste and de-ionised water, was undertaken on composite samples recovered from the Greendykes and Drumshoreland oil shale waste. These results indicate that the waste is not inert, and small but significant increases in dissolved chemistry were recorded, however as the data are not comparable to the natural mine water discharges sampled in the catchment they are

not included in the characterisation in this chapter. The analysis data is available in the Appendix.

6.4 Water analysis

Mine waters sampled in the field were sent to British Geological Survey (BGS) UKAS accredited Analytical Geochemistry Labs in Keyworth for analysis. Major and trace elements were determined by inductively coupled plasma mass spectroscopy, ICP-MS. Selected anions (Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , Br^- , F^- , HPO_4^{2-}) were determined using ion chromatography (Test procedure AGN 2.3.6) and pH and alkalinity, in addition to field analysis or where field analysis could not be undertaken, were determined by potentiometric titration (AGN 2.3.7). Full analysis report data is presented in Appendix C.

6.5 Analysis results

The locations of the twenty six mine water discharges sampled in the catchment are displayed below in Figure 6.2; the corresponding chemical analysis data are presented in Table 6.2.

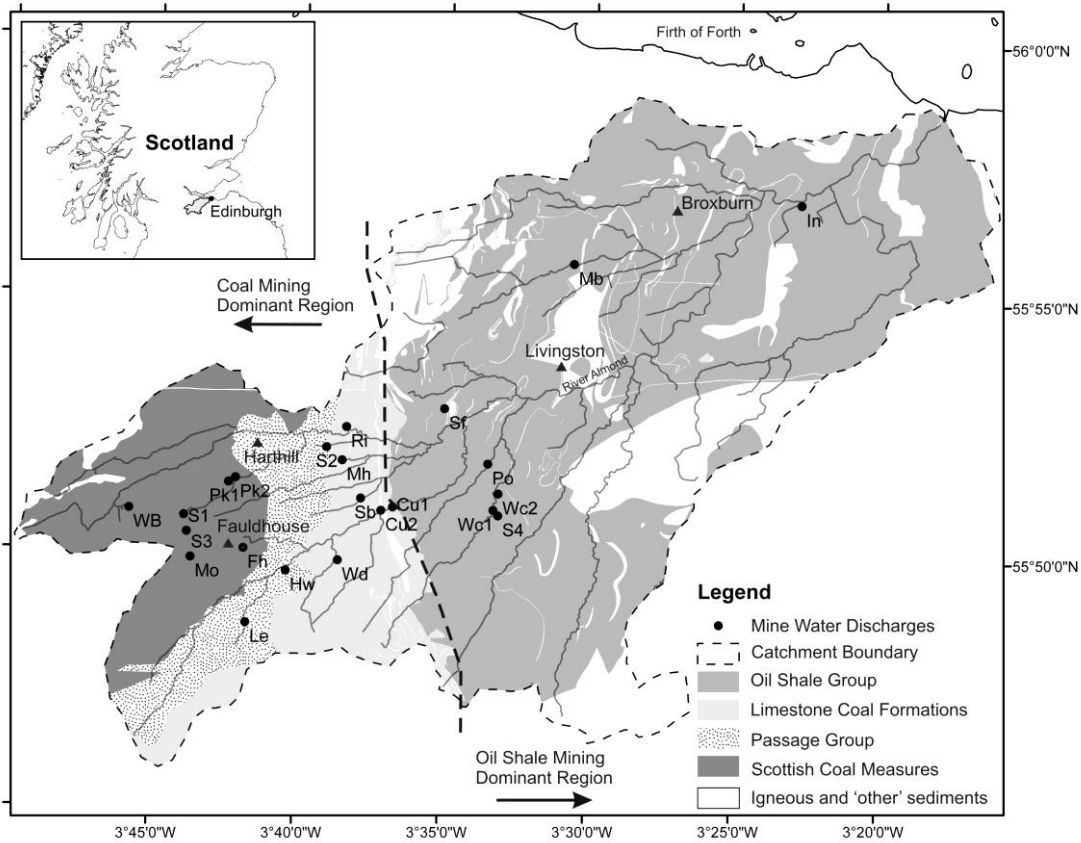


Figure 6.2 - Sampled Mine Waters in the Almond River Catchment- abbreviations used are consistent with those used in Table 6.2 and the mine water classification figures. In total 23 mine site discharge waters were sampled and analysed.

Discharge Name	Abb	Source	Temp (°C)	pH	Cond. (µs/cm)	Fe	Fe ²⁺	Fe ³⁺	Mn	Al	Ac.	Alk.	Net Alk.
Polkemmet Moor	S1-N	I	10	3.3	1268	129.0	125.2	3.9	14.2	6.558	321.4	0.0	-321.41
Polkemmet Moor	S1-NE	I	9.5	2.2	2170	158.7	70.4	88.3	19.4	4.006	735.2	0.0	-735.21
West Benhar	WB	I	-	2.6	-	47.7	-	-	18.8	49.200	533.0	-	-533.00
Whitrigg	S2	C	8.9	6.2	1697	78.6	67.3	11.3	12.1	0.061	172.8	154.1	-18.72
East Benhar	S3	C	7.9	5.9	382.0	0.4	1.058	0.0	0.3	0.067	2.8	81.1	78.31
East Benhar	S3	C	12.2	6.7	243.0	1.0	0.951	0.1	0.1	0.074	2.4	112.0	109.66
Moss	Mo	C	9.1	8.8	188	2.9	0.000	2.9	0.5	1.400	16.5	0.0	-16.45
Fauldhouse	Fh	C	10.2	6.2	255	3.7	0.000	3.7	0.4	0.500	13.4	11.2	-2.26
Moss Hall Farm	Mh	C	9.1	7.5	373	0.8	0.016	0.8	0.8	0.030	3.8	99.2	95.34
Stoneyburn	Sb	C	5	8.2	2900	0.7	0.000	0.7	10.7	0.100	21.9	0.0	-21.89
Seafield	Sf	OS	14.2	7.11	368	4.4	0.04	4.3	1.6	0.089	15.2	99.7	84.57
Hermand	S4	OS	5.5	6.8	527	1.4	1.1	0.2	3.3	0.025	8.8	187.7	178.88
Hermand	S4	OS	13.0	6.5	353.0	2.4	0.9	1.5	0.5	0.154	7.3	127.0	119.75
Polbeth	Po	OS	9.4	7.9	1018	0.8	0.0	0.7	0.2	0.070	2.8	286.1	283.34
Cuthill1	Cu1	CM		5.5	1990	37.0	-	-	0.9	0.100	68.4	247.0	178.65
Cuthill 2	Cu2	CM	10.7	7.7	1004	37.9	0.0	37.9	3.0	0.028	107.2	77.4	-29.76
Woodmuir	Wd	CM	10.3	7.3	849	41.6	0.7	40.9	3.2	0.015	116.7	200.0	83.26
Levenseat	Le	CM	8.3	7.8	656	10.4	0.3	10.1	1.7	0.321	32.6	35.2	2.67
Polkemmet	Pk1	CM		7.16	1080	21.8	21.3	0.5	9.6	-	57.0	341.0	284.04
Polkemmet	Pk2	CM	19.2	6.83	2230	48.6	21.72	26.88	3.085	0.007	116.44	463.93	347.50
E. Handax Wood	Hw	CM	-	6.9	425	17	-	-	-	-	-	-	-
Riddochill	Ri	CM	-	6.66	3380	20.8	20.8	0.0	8.3	-	52.2	368.2	315.94
West Calder1	Wc1	OSM	6.9	6.3	855	1.4	1.4	0.0	1.0	0.016	4.3	232.8	228.44
Ingliston	In	OSM	12.6	6.34	617	0.4	0.4	0.0	0.4	0.001	1.5	168.0	166.56
West Calder 2	Wc2	OSM	13.4	6.66	296	3.3	3.3	0.0	0.4	0.017	6.7	136.9	130.20
Millers Bridge	Mb	OSM		6.7	630	2.7							

Discharge Name	Abb	Source	Ca	Mg	Na	K	HCO ₃	Cl	SO ₄	NO ₃	Cl/Cl+SO ₄ (meq)	Lab Ionic Balance
Polkemmet Moor	S1-N	I	118.3	12.3	11.5	0.6	0.0	12.3	490.2	1.0	0.03	11.75
Polkemmet Moor	S1-NE	I	170.1	17.7	10.9	0.6	0.0	11.5	807.0	1.9	0.02	4.75
West Benhar	WB	I	-	-	-	-	-	-	1716.0	-	0.00	-
Whitrigg	S2	C	217.3	52.4	6.9	10.7	188.0	6.0	669.1	1.4	0.01	5.6
East Benhar	S3	C	18.2	13.1	3.9	42.7	99.0	28.5	13.5	1.5	0.74	9
East Benhar	S3	C	23.8	18.0	4.6	2.7	136.7	5.1	20.8	0.5	0.25	2.8
Moss	Mo	C	6.5	2.14	4.2	15.7	0	20.3	39.3	0.0	0.41	-4.9
Fauldhouse	Fh	C	22.5	3.76	12	2.2	13.644	18.3	63.7	0.2	0.28	3.7
Moss Hall Farm	Mh	C	35.2	9.03	5.2	40.9	120.98	45.1	15.7	0.8	0.80	3.4
Stoneyburn	Sb	C	425.1	148.89	13.3	110.7	0	79.0	1851.8	11.8	0.05	-4.7
Seafield	Sf	OS	44.5	8.3	19.7	2.87	121.66	29.2	22.4	3.8	0.64	9.75
Hermant	S4	OS	64.8	10.94	13.3	62.47	229	42.9	23.2	6.4	0.72	8.8
Hermant	S4	OS	51.4	8.46	14.3	23.77	155	15.4	26.2	9.7	0.44	7.3
Polbeth	Po	OS	123.3	21.48	52.5	19.2	349.1	80.8	96.6	27.5	0.53	1.4
Cuthill1	Cu1	CM	345	97	75	15	301.34	40.0	932.0	-	0.05	-
Cuthill 2	Cu2	CM	94.4	28.26	16.8	6	94.5	24.1	301.0	0.2	0.10	-3.6
Woodmuir	Wd	CM	99.4	25.92	8.8	15.1	244	18.5	164.9	0.1	0.13	2
Levenseat	Le	CM	69.4	23.75	10.8	5	43	17.8	255.0	0.9	0.09	0.8
Polkemmet	Pk1	CM	102	55.3	97	19.9	416.02	30.3	1036.5	-	0.04	-
Polkemmet	Pk2	CM	262	217	63	25	566	13.8	1377	0.02	0.01	-
E. Handax Wood	Hw	CM	-	-	-	-	-	-	-	-	-	-
Riddochill	Ri	CM	345	242	49.8	20.95	449.1552	27.4	1565.0	-	0.02	-
West Calder1	Wc1	OSM	73.7	14.35	31.8	65.83	284	57.2	16.7	24.6	0.82	-
Ingliston	In	OSM	79.6	19.41	22.3	2.66	205	35.6	109.1	4.2	0.31	-0.56
West Calder 2	Wc2	OSM	39.7	6.66	10.4	3.17	167	6.3	15.2	1.4	0.36	-0.2
Millers Bridge	Md	OSM	-	-	-	-	-	-	-	-	-	-

Table 6.2 - Major ion and selected trace element analysis of 26 samples from Almond mine waters. Ac.= Acidity (this has been calculated using eq.1 except when shown in bold, in this case they were provided by the data source), Alk.= Alkalinity as CaCO₃, Net Alk= Net Alkalinity as CaCO₃, calculated by Alk-Ac. Where Fe²⁺, Fe³⁺ are shown in *bold italics* they have been calculated in PHREEQC using the WATEQ4F database. I=ironstone mine waste, C=coal mine waste, OS= oil shale waste, CM= flooded coal mine, OSM= flooded oil shale mine

6.7 Classification of Almond Mine Waters

The piper, mine water pH-Fe and Alk vs. SO_4 classification schemes, as described in Chapter 2, have been used to examine the mine water samples, representing different mine sites types, in the Almond River Catchment. The chemical parameters calculated to achieve this are presented in Table 6.2 and the resulting diagrams are displayed in Figure 6.3. The MAMDI mine water hazard classification scheme as described in Chapter 2 has also be used to classify the mine waters the result of the this are shown in Table 6.3

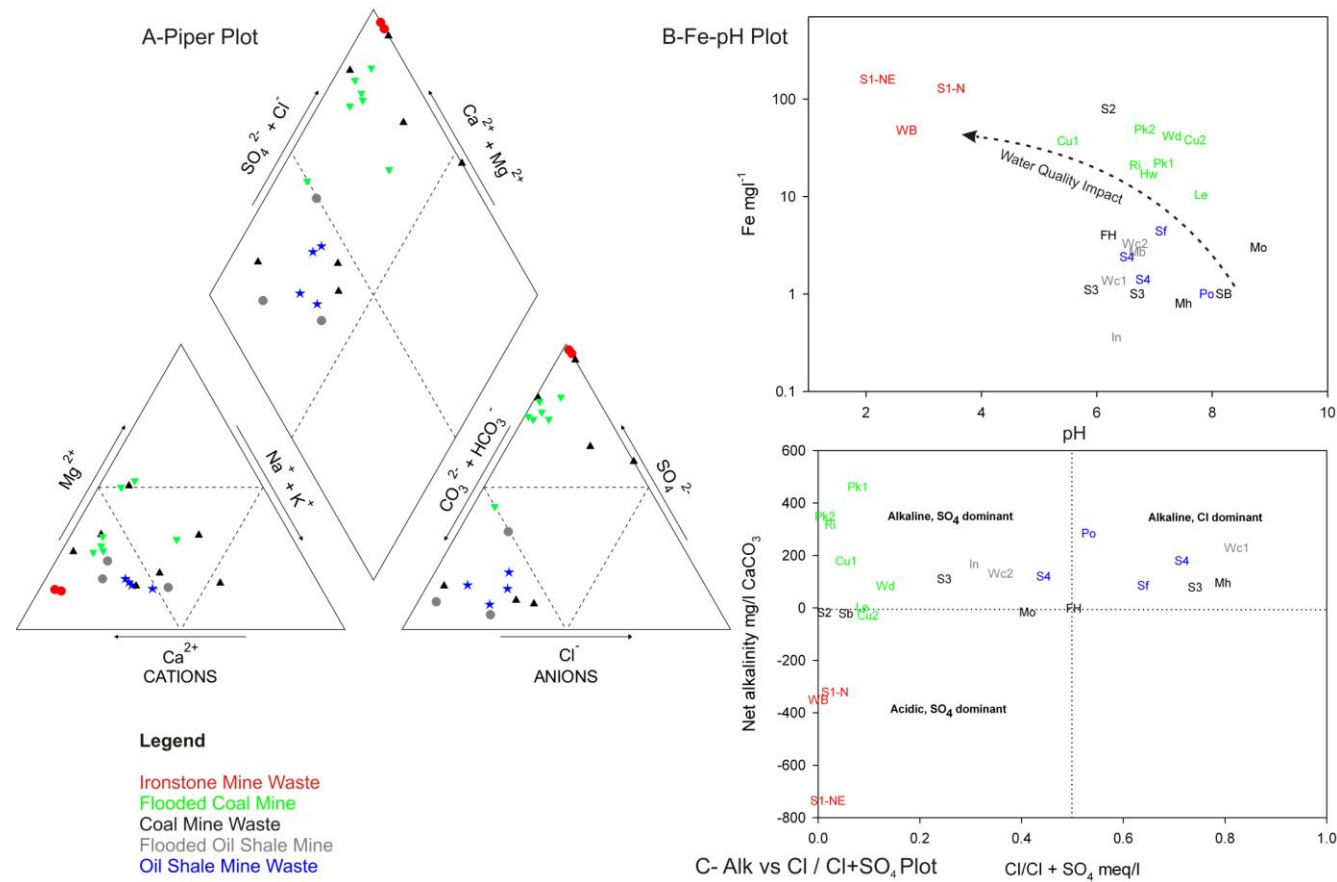


Figure 6.3 - Almond mine waters classified using groundwater and mine water classification schemes. A- shows the sampled mine waters using the Piper classification scheme. B- shows the sampled mine waters on a Fe-pH plot, C- shows the sampled waters on the Younger 1995-Rees et al. 2002, alkalinity vs sulphate dominance plot.

		Group 1		Group 2		Group 3		Group 4		MAMDI	
Site	Source	pH	SO ₄ ²⁻	Fe	(Cu, Zn)	(Al, Ag, Ba, Mn)	(Pb, As, Se, CN, Cr, Mo, Ni, Sb, U)	(Be, Cd, Hg, Tl)	Σ(Scores)	(Σ(Scores)) ²	(Σ(Scores)) ² /100
S1-N	I	9	21	9	10	4	8	9	70	4900	49
S1-NE	I	3	18	9	10	4	8	9	61	3721	37.2
WB	I	6	14	11	10	3	10	10	64	4096	41.0
S2	C	19	19	10	9	4	8	10	79	6241	62.4
S3	C	18	25	15	10	10	10	10	98	9604	96.0
Mo	C	20	25	14	10	7	10	10	96	9216	92.2
Fh	C	19	25	14	10	8	10	10	96	9216	92.2
Mh	C	14	28	15	10	8	10	10	95	9025	90.3
Sb	C	20	14	15	10	4	9	10	82	6724	67.2
Sf	OS	20	25	14	10	7	10	10	96	9216	92.2
S4	OS	20	25	14	10	6	10	10	95	9025	90.3
Po	OS	20	25	15	10	9	10	10	99	9801	98.0
Cu1	CM	16	18	11	10	8	10	10	83	6889	68.9
Cu2	CM	20	23	11	10	6	9	10	89	7921	79.2
Wd	CM	20	25	11	10	6	9	10	91	8281	82.8
Le	CM	20	24	12	10	7	8	10	91	8281	82.8
Pk1	CM	20	24	14	10	7	10	10	95	9025	90.3
Pk2	CM	20	16	11	10	6	10	10	83	6889	68.9
Ri	CM	20	15	12	10	5	10	10	82	6724	67.2
Wc1	OSM	19	25	14	10	8	10	10	96	9216	92.2
In	OSM	19	25	15	10	9	10	10	98	9604	96.0
Wc2	OSM	20	25	14	10	9	10	10	98	9604	96.0

Table 6.3- Modified acid mine drainage index calculation table for the sampled mine waters in the Almond Catchment. The mine waters are assigned hazard ranks based on the concentrations of different chemical and chemical groups shown across the top of the table. These are combined to give an overall MAMDI value which ranges between 1 and 100, with 1 being the most severe and 100 the least. (Where scores are in *italics* these have been presumed due to a lack of historic data for metals and metalloids)

6.7.1 Ironstone Mine Waste

The sampled ironstone mine waste discharge waters show a dominant Ca-SO_4 signature, have low pH (2-3), contain significantly elevated Fe concentrations (up to $\sim 160\text{mg l}^{-1}$) and have the greatest pollution potential of all the sampled waters plotting in the 'Acidic and SO_4 dominant' region of Figure 6.3C.

The Ca-SO_4 signature and high Fe concentrations indicate that pyrite oxidation and carbonate buffering exert significant control over the evolution of discharge waters, however, the low pH of the waters indicates that acid production dominates over buffering processes. This was demonstrated by the inverse modelling for site S1 in Chapter 5. The excess of acidity produced at the mine waste sites is due to the high pyrite and jarosite content of the ironstone wastes and the continual availability of oxygen and oxygenated rainwater at the mine waste site.

The concentrations of Fe, Mn, Al and Ni are all above nationally and internationally recognised drinking water (World Health Organisation) and surface water environmental quality standards (WFD Values) and represent a significant hazard to surface water and groundwater. The formation of significant volumes of Fe and SO_4 precipitates has been documented at both sampled ironstone sites. Precipitate formation reduces the availability of dissolved oxygen and causes further reductions in pH in surface waters. Transport of dissolved Fe downstream and the re-suspension of Fe precipitates under increased flow will contribute to the elevated Fe concentrations and Fe flow dependence in the Almond River waters (Chapter 4).

The calculated MAMDI values of 37-49 are the most severe of all the sampled waters in the catchment.

6.7.2 Flooded Coal Mines

The piper plot indicates that the flooded coal mine waters have a dominant SO_4^{2-} anion signature but a more variable cation signature varying between Ca^{2+} , Mg^{2+} and no dominant anion. All the waters contain $\text{Fe} > 10\text{mg l}^{-1}$ (with the highest value of

48.6mg l^{-1} recorded at Polkemmet, Pk2) have near neutral pH (5.5-7.8) and generally plot as 'Alkaline and SO₄ dominant'; Levenseat plots as slightly acidic.

The SO₄ dominance and elevated Fe concentrations indicate pyrite oxidation to be significant in the evolution of mine waters. However, unlike with the ironstone sites carbonate buffering is sufficiently dominant to maintain near neutral pH, giving the waters a net alkaline nature. This is due to high availability of carbonate minerals within the mined strata of Lower and Middle Scottish Coal Measures and Limestone Coal Groups in the catchment. Pyrite and carbonate buffering were modelled as the dominant processes operating at Polkemmet, Pk, by Chen et al (1999).

Concentrations of Fe and Mn in all the samples and Al and Ni at Levenseat, Le, are above drinking water and environmental quality standards indicating them to be of significant hazard to surface and groundwater. The formation of Fe precipitates was recorded at all of the sampled discharges, which will impact surface water pH, dissolved oxygen levels and contribute to the disperse and flow dependent nature of Fe in catchment river waters. These sites, being in direct contact with regional groundwater, will directly impact groundwater quality. Indirect impact may also occur through surface water- groundwater interactions.

The calculated MAMDI values range of 67-90 indicates the potential mine water hazard to be significant but variable.

6.7.3 Coal Mine Waste

Coal mine waste discharge waters show variable cation signature and an anion signature that varies between HCO₃ and SO₄. Dissolved metal content is also variable with high Fe, 78.6mg l^{-1} , at Whitrigg and high Mn, 10.7 mg l^{-1} , at Stoneyburn, while the rest of the sites generally have significantly lower values, particularly compared to the ironstone mine waste or flooded coal mine sites. The pH of sampled water varies between 5.9 and 8.2. The mine water classification in Figure 6.3C ranges from 'Acidic and SO₄ dominant' (S2 and Sb) to 'Alkaline and Cl dominant' (S3 and Mh).

The variable nature of the discharge chemistry is due to the variable lithological and mineralogical nature of coal mine waste. Any waste produced from the progression of a coal mine, which can include sandstone, mudstone, seat earth, limestone and marl, is termed a coal mine waste. The sulphate dominance and elevated dissolved metals contents in, S2 and Sb, is indicative of significant pyrite oxidation. The range of lower SO_4 dominance through to Cl dominance, together with slightly elevated Fe, is indicative of limited to negligible pyrite oxidation at the other sites. Carbonate buffering or accelerated weathering of calcite, dolomite and feldspar in the wastes results in the majority of the discharges being alkaline.

Although the chemistry of the coal mine waste discharge waters is variable, almost all the sites discharge Fe and Mn at concentrations above drinking water and environmental quality standard values. The formation of Fe precipitates at the sites was variable, at S2 Fe ochre formation was significant, it was also significant at Sb which is somewhat contradictory to the low $\text{Fe}-0.77\text{mg l}^{-1}$ recorded. Fe precipitate formation at the other sites was apparent but less significant.

The calculate MAMDI values vary from 62-96 indicating the potential mine water hazard to be significant but variable.

For the purpose of hazard map construction (Section 6.5) coal mine wastes have been split into two mine site categories. S2 and Sb have given a more severe hazard rank than other sites in the catchment. This may underestimate other coal mine sites in the catchment which also contain significant pyrite, AGS content, and discharge waters with low MAMDI values; however, this is unlikely to make a significant impact on the hazard map hazard classes. It is clear that the in future the term 'coal mine waste' maybe inadequate for the association of hazard for hazard mapping because of the variable lithological and mineralogical nature of coal waste. Most coal mine sites described in the literature are those which have high pyrite content and discharge significantly contaminated waters because these are the features which make the sites of scientific interest. However, there are many sandstone dominant coal mine wastes,

such as East Benhar, S3, which pose lesser threat to the water environment than the term coal mine waste might imply.

6.7.4 Flooded Oil Shale Mine

The sampled flooded oil shale mine waters generally show a Ca-HCO_3 signature, have slightly elevated dissolved metal contents, $\text{Fe} < 4\text{mg l}^{-1}$, near neutral pH 6.3-6.7 and vary between 'Alkaline and SO_4 moderate' to 'Alkaline and Cl dominant'. These chemical features suggest that pyrite oxidation exerts only limited influence on the mine water chemistry, this is likely to be due to the majority of the mines having been flooded for over 50 years and some of the sites for up to 150 years. Significant oxidation reactions will be limited to the zone of seasonal groundwater fluctuation. Also although coals and oil shale contain similar sulphur and pyrite content, the rocks of the Oil Shale Formation are generally significantly more arenaceous and likely to lack high pyrite content compared to the Scottish Coal Measures.

Fe and Mn concentrations in the sampled waters are generally above drinking water and environmental quality standards and as such may represent a threat to the surface water and groundwater environment. Fe precipitate formation was observed at all the sampled flooded oil shale sites indicating that the discharges contribute to elevated Fe concentrations in the Almond surface waters.

The calculated MAMDI values range of 92-96 are amongst the lowest of all the mine waters sampled in the catchment indicating them to be of limited potential hazard. However the diffuse influence of Fe from oil shale mines in the oil shale dominant mining regions of the catchment is significant (Chapter 4)

6.7.5 Oil Shale Mine Waste

The sample oil shale mine waste waters show a Ca-HCO_3 signature, contain Fe up to 4.4mg l^{-1} and are generally alkaline and chloride dominant. The majority of wastes, being orangey red processed oil shale are depleted in pyrite, compared to other mine waste rocks, due to the industrial processing in the Shale Oil Industry. The lack of a

significant SO_4 content is consistent with this while the slightly elevated Fe content may be related to weathering of hematite or more probably due to oxidation of limited pyrite content in the unprocessed black shales encountered at most oil shale waste sites (Chapter 3 & 5). The calcium and bicarbonate content of the waters is related to significant carbonate mineral content (Chapter 3). The Cl dominance of the wastes could be explained by the residual flushing of Na-Cl pore waters from the black unprocessed shales, this has been shown to occur in similar shaley wastes elsewhere in the UK (Banks et al. 1997b). However, no significant Na component is recorded in the majority of the samples.

As with the flooded oil shale mines, Fe and Mn concentrations are generally above drinking water and environmental quality standards and as such may represent a threat to the surface water and groundwater environment. Compared to ironstone mines waste sites or flooded coal mine sites the potential threat is limited. Fe precipitate formation was observed at all the sampled discharges indicating that the discharges contribute to elevated Fe concentrations in the Almond surface waters. The size of the oil shale waste sites and the lack of identifiable discharge streams at most of the sites suggest the wastes may represent a diffuse groundwater pollution risk due to significant downward movement of waters containing moderately elevated Fe concentrations.

The calculated MAMDI values range 90-98 are similar to the flooded oil shale mines indicating them to be of limited potential hazard.

6.7.6 Mine water Classification Summary

Table 6.4 summarises the chemical and hazard assessments for each of the mine water sources categories. Clear trends can be identified associated with different sources of mine water in the catchment and the source types represent a range of potential water quality hazard. This chemistry and hazard classification has been used to assign the differing mine site hazard ranks (Table 6.4 and Figure 6.4).

	Piper Classification	pH	EC ($\mu\text{S}/\text{cm}$)	Fe mg l^{-1}	Net Alkalinity as CaCO_3 mg l^{-1}	SO_4 Dominance	MAMDI	Mine Site Hazard Rank
Ironstone Mine Waste	Ca- SO_4	2-3	740-2200	30-160	-750 to -150	Yes	37-49	5
Coal Mine Waste	SO_4 , HCO_3^-	5.9-8.2	180-2900	0.5-80	-25 to 110	Variable	62-96	3 - 4
Oil Shale Mine Waste	Ca- HCO_3^-	6.5-7.9	350-1020	0.8-4.4	80 to 300	No	90-98	2
Flooded Coal Mine	Ca- SO_4 , Mg- SO_4	5.5-7.8	425-3380	10-50	-30 to 350	Yes	67-90	4
Flooded Oil Shale Mine	Ca- HCO_3^-	6.3-6.7	296-855	0.5-3	130 to 230	Variable*	92-96	2

Table 6.4 - Summary of mine discharge classification in the Almond River Catchment. The mine water source types are shown relative to the main geochemical parameters and classification methods. These parameters are then give an indicative severity colour rating with red representing the most significant chemical hazard and green the least. An overall mine hazard rank on the right has been assigned to each source type.

A colour coded ‘traffic light’ system (red-high impact, orange- moderate, green- low) has been used to identify the chemical features which are considered to represent significant hazard to the water environment. The ‘Mine Site Hazard Rank’ has then been assigned based on mine water classification and MAMDI values. These features are also summarised in Figure 6.4.

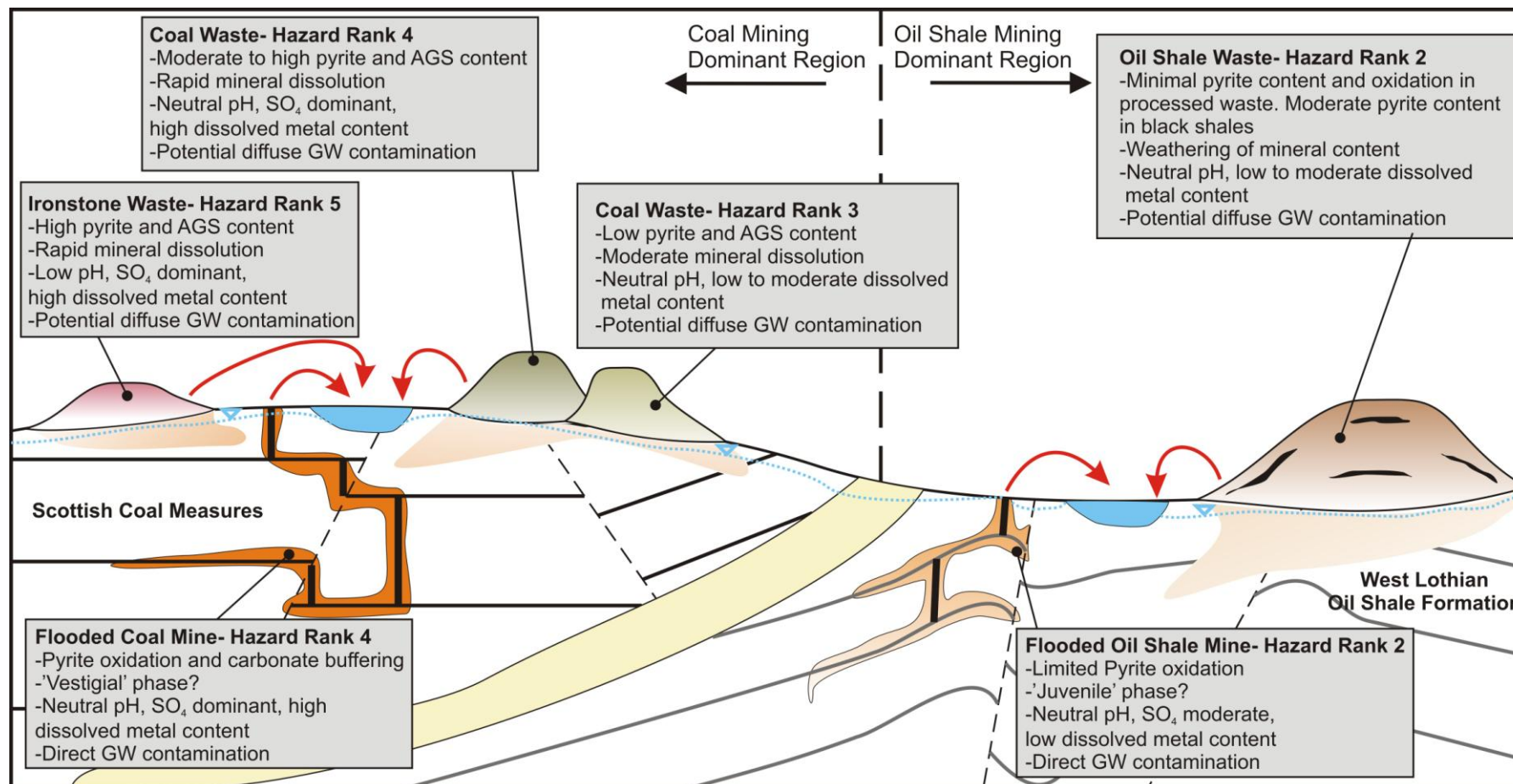


Figure 6.4 - Almond Catchment mine water hazard conceptual model. The model shows the different mine site types in the catchment in a diagrammatic representation and a summary of the main geochemistry and discharge hazards.

6.8 Hazard map construction

The mine water and hazard characterisation methods and principles presented in this chapter allow the development of a preliminary mine water hazard map for the Almond Catchment. The 'Mine Site Hazard Rank' presented in Table 6.4 is used to calculate different hazard classes associated with the density and prevalence of mining in sub-catchment areas with the Almond Catchment. Outlined below is the hazard map construction methodology;

- 1. Sub-Catchment Definition-** This was achieved using Low Flow Enterprise (LFE) Version 6.2 SEPA (Software Copyright © Wallingford HydroSolutions Ltd 2012). LFE allows the accurate definition of small sub-catchment areas using a digital terrain model. Initially water bodies with catchment areas above 10km² were selected. In areas where mine density was very high, namely along 'Breich Water', smaller sub-catchment areas were selected to increase the surface water hazard resolution. In total 40 surface water stretches were selected (Figure 6.5). Sub-catchment area shapefiles are created in LFE using a climb model from the catchment pour points, together with a flow estimation. The shapefiles were then imported into ArcGIS.
- 2. Mine Site Association-** Using the imported shapefiles the number of each mine site type within the 40 defined areas was counted. In this case this was done manually because it was considered to be the most time efficient method, however, on a larger regional or national scale, when manual counting would be excessively time consuming, a counting function could be created using a stepwise model of Arc Toolbox analysis tools in ArcGIS.

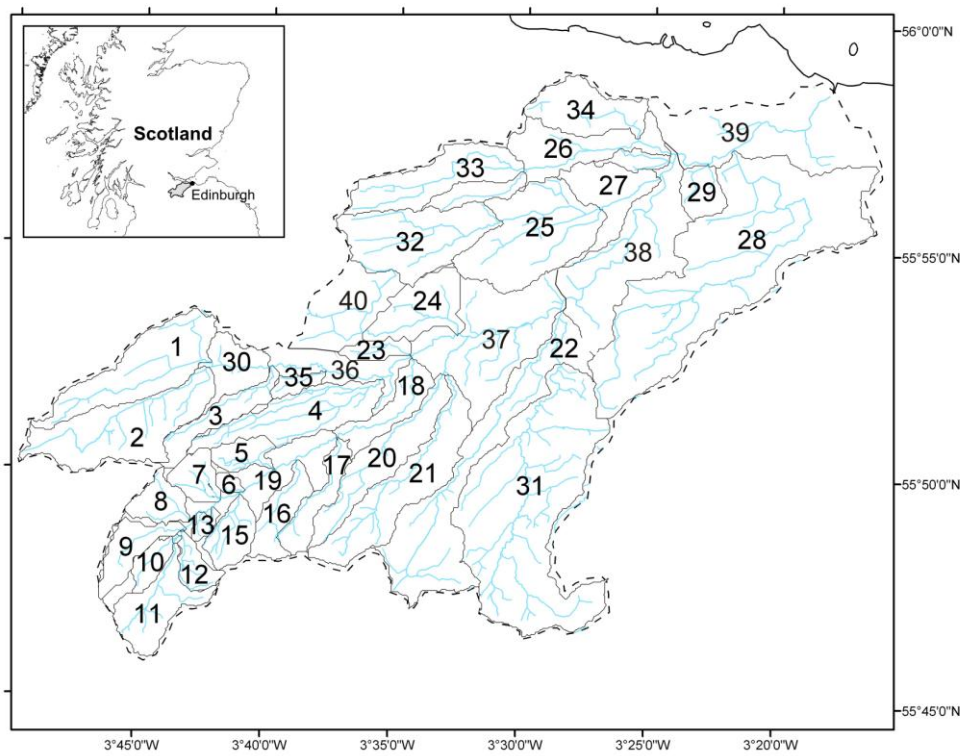


Figure 6.5- Hydrometric area definition for hazard map construction. The catchment has been divided into 40 sub-catchments using LFE and a digital terrain model.

- 3. Sub-Catchment Hazard Rank-** Each mine site was attributed the 'Mine Site Hazard Rank' outlined in Table 6.4; the sum of this was then calculated for each sub-catchment area (Table 6.5).

Name	No.	Catchment area	Coal	Coal Waste Type 1	Coal Waste Type 2	Ironstone	Oil Shale	Oil Shale Waste	Coal Hazard	Coal Waste Hazard (1)	Coal Waste Hazard (2)	Ironstone Hazard	Oil Shale Hazard	Oil Shale Waste Hazard	Σ (Mine Site Hazard Rank)	Hazard Class
Muldron Wood 1	13	0.7	0						0	0	0	0	0	0	0	Green
Ingliston	29	3.24					1		0	0	0	0	2		2	
R.Almond D/S of Airport	39						1		0	0	0	0	2	0	2	
Gogar Burn	28	48.71					1	1	0	0	0	0	2	2	4	
Lingore Linn	9	4.37	2						8	0	0	0	0	0	8	
Linhouse Water	31	40.79					3	1	0	0	0	0	6	2	8	
Seafield Burn	23	1.98					6	1	0	0	0	0	12	2	14	
R.Almond D/S of Oakbank	38	38.14					6	1	0	0	0	0	12	2	14	
Latchburn	35	1.37	2	1	1				8	4	3	0	0	0	15	
Muldron Wood 2	14	0.18	3		1				12	0	3	0	0	0	15	
Swine Burn	34	7.91					5	3	0	0	0	0	10	6	16	
Kitchen Linn	10	2.38	5						20	0	0	0	0	0	20	
Broxburn	27	7.08					6	4	0	0	0	0	12	8	20	
R.Almond D/S of Breich Water	37	20.8					9	1	0	0	0	0	18	2	20	
East Badallan	8	3.38	6		1				24	0	3	0	0	0	27	Yellow
R.Almond D/S of Whitburn	36	6.57	7						28	0	0	0	0	0	28	
Harwood Water	24	7.58					13	1	0	0	0	0	26	2	28	
Darmead Linn	11	7.29	5		3				20	0	9	0	0	0	29	
West Calder Burn	21	13.87					11	4	0	0	0	0	22	8	30	
Breich Water U/S W. Calder	19	11.73					13	2	0	0	0	0	26	4	30	
Croftfoot Burn	6	0.7	7		1				28	0	3	0	0	0	31	
Broxburn @ Dechmont	32	13.76					16	1	0	0	0	0	32	2	34	
Niddry Burn	26	10.5					15	3	0	0	0	0	30	6	36	
Ecclesmachan Burn	33	13.22					16	3	0	0	0	0	32	6	38	
Almond U/S Whiteburn	30	4.84	8		3				32	0	9	0	0	0	41	Orange
Starlaw Burn	20	9.71					17	4	0	0	0	0	34	8	42	
Beugh Burn	25	16.89					19	6	0	0	0	0	38	12	50	
Muldron Burn	12	3.01	12		1				48	0	3	0	0	0	51	
Howburn	1	13.43	13						52	0	0	0	0	0	52	
Murieston Water	22	21.49					22	4	0	0	0	0	44	8	52	
Bickerton Burn	4	11.01	11	1	3				44	4	9	0	0	0	57	
Cultrig Burn	3	6.06	12		2	1			48	0	6	5	0	0	59	
Woodmuir Burn	16	4.52	14		2				56	0	6	0	0	0	62	
Holehose Burn	5	2.9	15		2				60	0	6	0	0	0	66	
Breich Water D/S W. Calder	18	7.57					34	6	0	0	0	0	68	12	80	Red
Longford Burn	17	4.4	23						92	0	0	0	0	0	92	
Green Burn	7	3.48	14		13				56	0	39	0	0	0	95	
Bankhead burn	15	3.99	29		6				116	0	18	0	0	0	134	
R.Almond to Howburn	2	15.23	34		2	2			136	0	6	10	0	0	152	
Total									888	8	123	15	428	92	1554	
% Total									57	1	8	1	28	6	100	

Table 6.5 – Mine water hazard calculation table. The table shows each of the sub-catchment areas defined in Figure 6.5. The hazard rank from Table 6.4 has then applied to each site and the total hazard rank for each area has been calculated.

4. Mine Hazard Class- The sum totals of the ‘Mine Site Hazard Rank’ were split into the Mine Hazard Classes as described in Table 6.6 below.

Σ (Mine Site Hazard Rank)	Hazard Class	Description
0-20	A-Limited	Small scale mining, probably shallow associated with limited or difficult to recover mineral resource. Mine water discharge may impact water quality in small and larger close proximity streams and burns.
21-49	B-Significant	Locally significant mining unlikely to include interconnected workings, mine waste volumes maybe significant, more so in oil shale areas. Mine water discharge may have significant water quality impact on small to large streams and burns. Possibility of cumulative diffuse impacts on sub-catchment and catchment water quality.
50-79	C-Important	Regionally and nationally (particularly for oil shale) significant mining may include interconnected subsurface workings and mine waste. Likely to contain several significant mine water discharges which may have impact on large streams and cumulative diffuse impacts on water quality throughout the sub-catchment, catchment and also to groundwater.
80+	D-Extensive	Nationally significant mining area likely to include deep interconnected subsurface workings and significant mine wastes volumes. High probability of numerous mine water discharges with cumulative diffuse water quality impacts throughout the sub-catchment, downstream in the main catchment and to regional groundwater.

Table 6.6 - Mine site discharge hazard class description- the table describes each of the hazard classes used in the mine water hazard map in Figure 6.6

6.9 Almond Catchment mine water hazard map

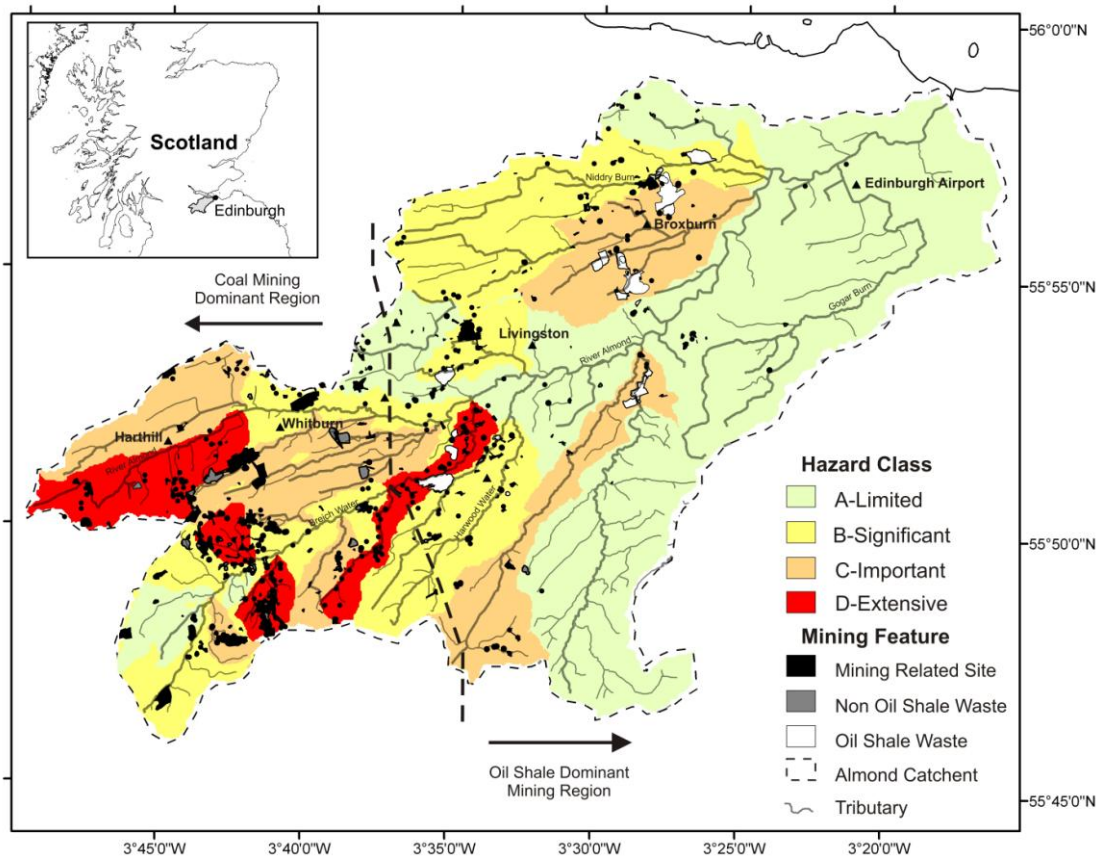


Figure 6.6 – Mine water hazard map of the Almond River Catchment. (an A3 size version of the Figure can be found in Appendix D). The colours on the map represent the potential mine water discharge hazard within sub-catchment areas based on sampling from a number of different mine site types within the catchment.

Environmental risk assessment is based principally on the Source-Pathway-Receptor concept; this concept is also reiterated in the EU WFD, as stated in Chapter 1. For a pollution linkage to be established then a source, a pathway and a receptor need to be present. Identifying pollution linkages in heavily mined areas on a site by site basis would present an extremely time consuming and laborious task.

- **The construction of the hazard map, using the individual mine site chemistry and hazard characterisation, defines the mining source potential within the Almond Catchment.**

The construction methodology also associates the source with the closest proximity surface water receptor. The map does not positively identify the pathway within the pollution linkage; however, the probability of a pollution linkage and associated impact being present, within a sub-catchment, is greatest where the mine density is highest i.e. in the 'D-Extensive' areas.

This hazard map and potentially others constructed using the same method will benefit assessment and prioritisation of actions associated with mine water management in addition to assessment, monitoring and potential remediation. Therefore, its principal users are likely to be environmental regulators (e.g. SEPA, EA), responsible parties such as the Coal Authority, local authorities (e.g. WLC) and interested parties such as research institutions (Universities and BGS). As a stand alone product it provides a preliminary assessment of mine water hazard based on accurate chemical evaluation of the range of mine water sources in the catchment. Primarily it indicates that the potential water hazard posed by the discharge of contaminated mine water from historic mine sites in the Almond Catchment is not uniform.

Five sub-catchment areas are classified as 'D-Extensive' on the map, indicating a high probability that surface waters are impacted by mine water discharge. Of these five areas, four are in the coal mining dominant region while one is in the oil shale mining dominant region. These areas correlate with the surface water Fe loading maps presented in Chapter 4; however the hazard map offers improved resolution of hazard. For example, the hazard map allows the identification of a number of small extensively mined areas along 'Breich Water'. The monitoring data in Chapter 4 only allows the identification 'Breich Water' itself as being impacted by mine water discharge. The hazard map could potentially be used to improved SEPA's monitoring network to identify and separate point and diffuse sources and impacts from historic mining, which was noted as priority for improved mine water management by Johnston et al. (2008) (Chapter 1).

Table 6.7 indicates that the five ‘D-Extensive’ areas occupy just 9% of the total catchment, yet these areas account for over 1/3 of the total hazard weight in the catchment. Conversely, 45% of the Almond catchment area is ranked as ‘A-limited’ indicating that reduced water quality in these areas is the result of either diffuse pollution from upstream mine sites or sources other than mining. Future investigations to improve mine site characterisation would clearly be of greatest benefit in the ‘D’ & ‘C’ Mine Hazard Class areas.

Mine Hazard Class	Σ (Sub-Catchment Area)	% Almond River Catchment
A- Limited	177.65	45
B- Significant	103.15	26
C- Important	79.31	20
D- Extensive	34.67	9
Total	394.78	100

Table 6.7 - Mine water hazard class by catchment area (in Km²) within the Almond River Catchment.

The hazard map can also be used as an indicator of direct and indirect groundwater pollution particularly when used in conjunction with the Scottish groundwater vulnerability maps (Ó Dochartaigh et al. 2005). This is of particular significance to the mine waste sites in the catchment. One potentially significant and currently poorly defined threat to groundwater comes from the downward movement of mine water, through mine waste, directly to groundwater via underlying superficial geology. Vulnerability maps consider the depth to groundwater, cover type and pathway permeability. Comparison of the hazard and vulnerability maps will allow for the identification of mine waste sites with the greatest potential to impact groundwater. However, many mine wastes, due to their size, cover historic mine adits and shafts, potentially producing a preferred pathway for the movement of water and significantly increasing groundwater vulnerability. This is thought to be occurring at the larger oil shale mine waste sites which cover several historic subsurface mine sites and also lack definite discharge streams at surface.

6.10 Limitations

There are a number of limitations which must be considered when interpreting the hazard map presented in Figure 6.6;

- The hazard classes are based on a worst case scenario which assumes that every historic mine site has the potential to discharge mine water to the surface water environment.
- The ‘mine site hazard ranks’ are assigned to grouped mine site types, however, no two sites within the same group will represent the same hazard. Therefore this will over represent some sites and under represent others.
- The mine site point or feature on the map may not represent the point of discharge of mine water. Therefore, a mine site in one sub-catchment area may discharge water some distance away, possibly, in a neighbouring sub-catchment area.
- The amount of mine water and consequently the mine contaminant volume discharged from a site can vary greatly. At this preliminary stage the hazard map does not represent this potential variability.

Nevertheless, the map identifies, through a scientifically based methodology, mined areas which pose the greatest threat to water quality. This information is useful for the assessment of hazards, prioritisation of actions and sampling in heavily mined areas.

6.11 Catchment management

The hazard map and mine site characterisation presented in this Chapter should help to improve the management of mine related water quality issues in the Almond Catchment, however, there are, in addition to scientific challenges, several legislative and practical challenges to overcome to improve catchment management. The principal parties and their respective responsibility associated with water quality impacts from historic mines in Scotland and the Almond Catchment are outlined in Table 6.8.

Issue	Responsible/Interested Party	Actions	Comments
Historic flooded coal mines	SEPA, CA	Establishment of a priority list of mine waters. Mine water treatment schemes.	Polkemmet and Cuthill were on the list; have since been removed due to treatment schemes being in place. No other mine water in the Almond on the list
Coal Mine Waste	WLC, SEPA (potential developers)	Treatment schemes in place at S2 and WB	No single strategy for dealing with impacts. Action tends to be based on pressure from local communities.
Historic flooded oil shale mines	SEPA, WLC	No treatment schemes in place	Low hazard. Unless high impact individual discharges are identified then an unresolved diffuse pollution issue
Oil Shale Mine Waste	SEPA, WLC	Some capped. Protected ecological status	Low hazard, potentially long term unresolved diffuse pollution issue
Ironstone Mine Waste	SEPA, WLC (University research)	WB-treatment scheme associated with university research	Treatment would be beneficial at S1- Polkemmet Moor Ironstone (Chapter 5). Identifying other ironstone sites would be useful
Water quality (from mining)	SEPA	Assessment as part of WFD	Impacts of mining could be better assessed with more targeted sampling and monitoring

Table 6.8- Mine water and water quality management in the Almond Catchment. The table describes and comments on the current regulatory response to each of the mine site types covered in this study and the impact on catchment water quality,

The Almond River Catchment being part of the wide Forth Basin is covered by the Forth River Basin Management plan (SEPA 2008) devised by SEPA as part of Scotland's legal environmental obligations under the EU WFD. The initial assessment stage of the management plan has already been undertaken and six out of the 21 baseline surface water bodies, in the Almond Catchment, were identified as

being under pressure from the impacts of historic coal and/or oil shale mining (SEPA 2011). This assessment largely ignores any potential impact from historic oil shale mining activities around Broxburn, Oakbank or Tarbrax as indicted by the Hazard Map. Also the WFD as part of SEPA's classification requirements simply identifies all those areas upstream of the Almond and Breich Water confluence as being under pressure from coal and oil shale mining. The hazard map offers improved resolution of hazard and, therefore, pressure in this area.

The principal aim of the WFD and subsequently the basin management plan is to improve water quality. Basin management plans under the WFD are cyclic and aims are outlined for achievement in one of three principal assessment cycle years, 2015, 2021 and 2027. The current catchment plan aims to reach good status for all 6 of the baseline surface water bodies with mining pressures, which are currently classified as poor, by either 2021 or 2027 (SEPA 2011). Contrary to this is the fact that no mine water discharges in the catchment are currently on the priority mine water list established by the CA and SEPA via a Memorandum of Understanding in 2001. Therefore, there are currently no plans for any new mine water treatment schemes in the catchment. Also, the priority mine water list does not cover mine waste discharge waters. The site two which originally were on the list, Polkemmet(Pk1+2) and Cuthill(Cu1), have been removed due to the construction of mine water treatment schemes. SEPA's River Almond Catchment Profile (SEPA, 2011) makes mention of delivering 'Pate's Mill/Baadsmill and Torphin Quarry' in negotiation with the CA, presumably this refers to mine water treatment schemes. Neither of these site names features on the priority mine water list obtained from SEPA in October 2012. Investigations over the last 4 years have not identified either of these mine sites within the catchment. It is thought that these appear in error and there is, therefore, no current plan for water quality improvement related to mine pollution in the catchment.

Improvements in water quality may be achieved due to improvements associated with other key pressures in the catchment such as sewage treatment and agricultural pollution. However, significant improvements in river level Fe concentrations which

average at above 2mg l^{-1} in some areas (Chapter 4) are unlikely without targeted mine water treatment schemes. The hazard map should aid in the selection of research and assessment areas which could highlight other priority discharges for potential remediation. Also the map can aid in improving SEPA's monitoring network in the catchment.

Mine waste is often the most obvious reminder of historic mining activities, particularly for the general public. The sampling investigation indicates that discharges from mine wastes containing high pyrite contents have significant local impacts on water quality. However, the number of mine wastes containing elevated pyrite content, i.e. ironstone and some coal sites, is a fraction of the total mine waste quantity in the catchment. Furthermore mine waste site frequency is subordinate to historic subsurface mine sites in the catchment. Further work might be necessary to properly represent mine waste as significant diffuse sources as the hazard map currently represents them as single point sources. The Environment Agency England and Wales (EA) have established an 'Inventory of Closed Mining Waste Facilities, 2012' as part of its legal obligation under 'The Mining Waste Directive, 2008'. As yet SEPA have not published a similar document. If an inventory for Scottish mine wastes was to be created it could be used to improve the hazard map and to characterise the mine waste on the national scale. Also a national scale inventory of mine waste sites could allow targeted sampling of different dominant lithology mine wastes to allow better characterisation of 'Coal Mine waste'.

6.12 Conclusions

A number of conclusions can be drawn about mine water chemistry and the resulting hazard in the Almond River catchment:

- Mine waters in the Almond River catchment show a range of chemistry and present significant potential hazard to the surface water and groundwater environment.
- Mineralogy is the principal control on mine waste discharge hazard, while abandonment age, reduced oxygen availability and lower pyrite content is

likely to be responsible for the lower mine contaminant concentrations in the flooded oil shale mine waters.

- The MAMDI values calculated for the different mine site categories allow for a relative rank of the mine site categories, however the categories themselves would benefit from further refinement. Particularly in the case of coal mine sites which show variable mineralogy and hazard. Investigations into the amount of unprocessed oil shale waste in the catchment would help to improve assessment of hazard.
- A hazard map based on an accurate definition of small catchment areas combined with a rigorous assessment of mine water chemistry allows the identification of key hazard areas in the catchment.
- Although the Almond Catchment is heavily mined 45% of the catchment area is categorised as 'A- Limited' indicating that mining and potential water impacts are limited while only 9% is categorised as 'D-Extensive'.
- The Hazard Map, although preliminary, should improve interpretation of water quality data in the catchment, identify ways in which the catchment could be more appropriately managed and highlight areas where further research would give considerable benefit to catchment management and future water quality improvement.
- Ambitious plans have been outlined as part of the implementation of the EU WFD to significantly improve surface water quality in the Almond Catchment. However, while it is well recognised that mine water contamination is a major issue in the catchment there are currently no plans to implement any new mine water treatment schemes. How significant improvements can be achieved particularly associated with river iron levels without any plans for mine water remediation currently appears to be an unknown.

Chapter 7

Summary, catchment model and further work

7.0 Introduction

This thesis provides a detailed assessment of the catchment scale impacts of historic mining industries and the processes of contaminant release to the water environment in the Almond River Catchment where coal, oil shale and ironstone were intensively mined for several hundred years. In doing so the thesis has reached a number of key findings:

- poor water quality is encountered in the majority of rivers in the Almond Catchment due to the cumulative impact of contaminated mine waters discharged from over 300 abandoned mine sites,
- the historic coal and oil shale industries produced a range of mine site types including mine wastes and flooded mines which show a range of different mine water chemistry and environmental impact,
- mine contamination in the surface water environment shows distinct diffuse behaviour heavily influenced by the prevailing hydrological conditions.
- The hazards posed by the complex and dense industrial mining industries in the catchment can be systematically characterised and mapped.

The characterisation of potential hazards from the different mine site types studied in the catchment has allowed for the development of a catchment wide mine water hazard map. This map, together with other findings from the thesis can be used to facilitate improvements to mine water monitoring networks in the catchment and prioritise actions for future mine water management. Furthermore, the study also

provides a template for a similar approach to mine water hazard mapping to be applied in other heavily mine catchments or on a national scale, possibly by an environmental regulator.

This Chapter presents a summary and discussion of the main thesis conclusions obtained through the completion of the objectives outlined in Chapter 1, provides a synthesis of the findings in a catchment conceptual model and outlines the potential for further work.

7.2 Summary and discussion of main findings

7.2.1 Oil shale

In Chapter 3 the historic oil shale industry was reviewed and data presented for the mineralogy and chemistry of a number of the oil shale wastes in the catchment. The oil shale industry was of huge significance to Scotland and, arguably, the world as for a short period in the 19th Century it resulted in Scotland becoming the world's largest oil producer (EASAC 2007). Not only has the significance of this industry in historic-economic terms been overlooked but also the need for an assessment of the potential environmental impact of the industry has been largely ignored.

Oil shale is a sedimentary rock with higher organic content, at approximately 10-12%, than most shales due to its deposition in a Carboniferous aged stratified anoxic lake which facilitated the preservation of organic material (Cadell 1925, Follows & Tyson 1998). An assemblage of approximately twenty oil shale seams is found in the Scottish Oil Shale Formation which outcrops in the Almond catchment (Cameron & Stephenson 1985). In 1851 James Young developed an industrial heating process which extracted the organic content of the shale as a form of crude oil (Redwood 1897, Louw & Addison 1985). The resulting industry was the world's first oil industry which mined and processed over 150 million tonnes of oil shale, with a total output of approximately 75million barrels of oil. The industry facilitated the economic and social development of West Lothian but struggled from the early 20th

century to compete with foreign imports of oil. In 1962 the final oil shale mine and processing facility was closed (Hallet 1985, Louw & Addison 1985).

A lasting legacy of the industry is ~150 mines worked in West Lothian of which the majority were located in the Almond Catchment, representing a worked area of over 4000ha in the subsurface (Mac Adam et al 1992). Peak production occurred in 1913 with the mining of 3.28 Mt, which is relatively modest compare to the peak production in the Estonian oil shale industry of 31Mt in 1980 (Katti & Lokk 1998). However, the Scottish Oil Shale Industry was the first in the world and pioneered many of the technological foundations for more modern conventional and unconventional hydrocarbon processing and exploitation (Hallet et al, 1985). It is estimated that the industry produced approximately 150 million tonnes of waste, which has been shown in other studies to be of ecological and economic value (Winter 2001, Harvie 2004) but the waste together with flooded oil shale mines are also of potential environmental concern to the water environment (Younger 2001, Robins 2002). Historic mineralogical and chemical data, principally pyrite and coal seam S content, were considered together with the geology of the West Lothian Oil Shale Formation to assess the potential impact of mine water discharge (Wood et al. 1999, Younger & Adams 1999, Younger 2000) from the numerous historic flooded oil shale mines in the catchment. This indicates that oil shale, found in the seam, contains pyrite and sulphur in quantities which are likely to lead to the discharge of contaminated mine waters. However, the Oil Shale Formation is generally more arenaceous than the coal bearing strata exploited in the neighbouring coal industry. This is likely to have led to lower concentrations of contaminants from oil shale mines than coal mines. This preliminary assessment acts as an indication of the need for further assessment of the impact of oil shale in West Lothian and elsewhere where oil shale mining has been undertaken such as Estonia, China, Australia and the USA (EASAC 2007). A sampling and characterisation exercise on a number of oil shale mine discharges is presented in Chapter 6 and is discussed below, however it is fair to say there is still a requirement for further national and global assessment of the environmental impacts of historic and present day oil shale mine discharges.

Oil Shale mine wastes, left behind from retorting practices, presents a potentially more complex scenario than flooded mines and a detailed understanding of the origins of the waste and its relationship to historic industrial processing is presented in Chapter 3. The processed orange red oil shale waste is found to contain significant hematite content (resulting in the red colouration), feldspar minerals, sheet aluminium silicates, carbonates and, in some cases, mullite and cordierite which are considered to be represent overheating of the waste either in the retort or by uncontrolled burning on the waste pile. This uncontrolled burning caused problems with air pollution and led to the fusing of the shale waste into large rock like fragments (Redwood 1897). This fusing is thought to be facilitated by the dehydration of feldspar and clay minerals and the formation of mullite and cordierite. Mullite and cordierite, therefore are the West Lothian equivalent of the ‘technogenic’ minerals from the Estonian carbonate oil shales wastes documented by Puura (1999). However, while the ‘technogenic’ minerals recorded in Puura (1999) are relatively reactive and may produce leachate discharges of environmental concern, mullite and cordierite are virtually inert (Deer et al. 1966, Schneider et al. 2008). This is thought to be related to the difference in mineralogical composition of the Scottish oil shale, which are clay dominant, and the Estonian oil shale, documented by Puura (1999), which are carbonate dominant. This suggests that the potential environmental impact of oil shale exploitation and waste is dependent on the oil shale reserve type since the term ‘*oil shale*’ has only a loose definition based on organic content and not on bulk mineralogy (Brendow 2003).

Neither pyrite nor any sulphate minerals are identified in the processed oil shale waste. Sulphur content is low and the waste is also lacking in nitrogen (Harvie 2004). However, sulphur in oil shale waste used as fill material has been implicated in steel corrosion (Winter & Butler 1999), one explanation for this is that because processed and unprocessed oil shale is found in most of the waste sites across West Lothian it is possible the fill used was in fact part unprocessed oil shale which contains a significant sulphur content (Bailey 1927). Comparison with the raw oil shale mineralogy indicates that the processing of the shale, to extract the organic content of the shale, fundamentally alters its mineralogical assemblage; iron in pyrite is

oxidised to form hematite, sulphur (which is present in unprocessed oil shale) is extracted with nitrogen to form ammonium sulphate and clay minerals are dehydrated forming feldspars and mullite and cordierite, as mentioned above. These findings are important because they indicate that historic processing reduced the potential environmental impact of the majority of the waste found in the Almond today primarily through the destruction of pyrite.

As mentioned above, evidence presented in Chapter 3 and Chapter 5 indicates that the oil shale waste sites, 'bings', although consisting predominantly of processed waste also contain a proportion of black unprocessed oil shale or blaes. This black unprocessed oil shale contains pyrite (Louw & Addison 1985) and is likely to contribute to diffuse contamination and high Fe loading described in Chapter 4. Unprocessed oil shale waste in Estonia also contains pyrite and is known to discharge Fe and SO_4^{2-} , however, because they are more carbonate rich they discharge waters which remain slightly alkaline due to an excess of buffering capacity and display a Ca, Mg major ion signature (Puura 1999). The West Lothian Oil Shales are clay shales and therefore have much lower carbonate content, however, because they are contained on mine waste sites dominated by processed shale (with no pyrite and up to 2% calcite) the potential for significant acidic discharge is also considered low. It is likely some localised acidic discharges on sites in West Lothian which are more dominant in unprocessed oil shale may occur.

The historic Scottish Oil Shale Industry has particular relevance today due to the rapid global move towards unconventional hydrocarbons. In the UK this could occur in the remaining down dip oil shale seams which were historically exploited as well as in Carboniferous and Jurassic ages shales (DECC 2011). Many concerns have been raised about modern day unconventional hydrocarbon exploitation (e.g. Osborn et al. 2011, The Royal Society and The Royal Academy of Engineering 2012, Haluszczak et al. 2013). The historic oil shale industry in West Lothian offers a worked example of unconventional hydrocarbon exploitation and associated modern day environmental impacts; 50 years after the closure of the industry. Although the mode of modern unconventional exploitation differs to the historic (deep drilling and

potentially hydraulic fracturing, compared to mining and retorting) many of the environmental issues are similar, i.e. how to manage process water, how to prevent uncontrolled release of hydrocarbons and the potential impacts of abandonment (The Royal Society and The Royal Academy of Engineering 2012). Therefore, understanding these historic environmental impacts helps to inform potential issues associated with modern day potential exploitation.

The processing of oil shale at historic retorting factories in the Almond had significant impacts on water quality due to the deliberate and accidental discharge of hydrocarbon contaminated water into the river system (Brock 1892). One of the main concerns surrounding modern day unconventional hydrocarbons is the management of hydrocarbon contaminated waters at surface. Indeed in America modern process waters are managed by surface lagoon storage which although lined are considered at risk from leaks, the use of closed system is expected in the UK (The Royal Society and The Royal Academy of Engineering 2012). Evidence also suggests the 100+ historic oil shale processing sites, in West Lothian, may have left behind a legacy of hydrocarbon ground contamination in the catchment which could potentially release hazardous substances directly to groundwater. Estonian oil shale wastes are known to be a source of hydrocarbon and phenol contamination (Seather et al. 2004). No assessment of hydrocarbon contamination has been undertaken within this thesis; this is an area where further study would be of benefit.

7.2.2 Water quality

In Chapter 4, a detailed examination of the distribution of historic mine sites in the Almond Catchment is presented utilising information provided by West Lothian Council, BGS and the Coal Authority supported by field investigations and historic information sources. The catchment is divided into a 'Coal dominant mining region' and an 'Oil Shale dominant mining region' based the subsurface geology and the availability of mineral resources. In total over 300 individual mine related sites are mapped.

An analysis of water quality datasets obtained from SEPA, dating back to 1994, reveals elevated concentrations of Fe and SO_4^{2-} at monitoring points on river tributaries throughout the catchment, indicating the deleterious influence of mine water discharge on water quality. A similar approach, using only one year of water quality data, was used to quantify the roles of diffuse and point source contamination in a heavily mined catchment in the North Pennines in North West England by Mayes et al (2008). Compared to that study the same focus on the separation of point and diffuse source was not undertaken here, although similar relationships in the Almond could be investigated, instead the aim here was to separate the oil shale and coal industries primarily because no detailed investigation of the water quality impact of oil shale mining had ever been undertaken (e.g. Younger 2001).

The water quality data from surface water monitoring sites across the Almond revealed median Fe concentrations that ranged $0.4\text{--}2.48\text{mgL}^{-1}$ and upper values consistently reaching approximately 3mgL^{-1} . These values suggest potential impacts on benthic invertebrate ecology in the Almond River and tributaries (Jarvis & Younger 1997), although no direct assessment of river ecology was undertaken in this study. After examination of the temporal variability of mine related contamination a second data set of flow data was obtained. Combining these data sets revealed significant flow dependence in the behaviour of Fe and SO_4^{2-} in the surface water environment. Fe is shown to increase with increased flow due to the re-suspension of diffuse river bed iron while SO_4^{2-} decreases with increased flow due to dilution. This flow dependent nature of mine related contamination is suggested in the Mayes et al. (2008) study however the data presented here offers a separate and more extensive case study on the flow dependent behaviour of mine related contamination in the surface water environment. This could have implications for the WFD classification of surface waters in heavily mined catchment across the UK, and potentially the whole of Europe, as environmental regulators do not normally consider the flow dependent nature of contaminant concentrations when classifying surface waters (SEPA 2008). Instead they use tend to use average concentration data which could significantly underestimate the significance of Fe precipitates in many river channels and also potentially underestimate the resulting ecological impacts.

Furthermore, precipitate or colloidal Fe within rivers also sorbs trace metals which are potentially more eco-toxic. While this sorption process limits the acute toxicity of trace metals to river ecology it does not eliminate it (Kimball et al. 1999). Therefore the sorption of eco-toxic metals such as aluminium, which would normally rapidly precipitate out of solution close to mine sites due to increases in pH (PIRAMID 2003, Younger & Sapsford 2004), on to Fe precipitates provides a viable route for transportation within river systems and to stream beds not considered to be directly at risk from AMD.

Surface water pH is also revealed to be influenced by flow, related to the change in river water source with groundwater input dominating at low flow and rain and surface drainage dominating at high flow. The resulting reduction in pH at high flow causes partial dissolution of the re-suspended Fe precipitates as the divalent Fe^{2+} species. This dissolution of Fe precipitates could potentially release any sorbed metals which may be more eco-toxic than Fe (Mayer et al. 1996).

A further analysis of flow and chemistry data sets allows the calculation of Fe load in surface waters. Increases in load are correlated with mined areas to give an indication of the areas where discharge of mine related contamination occurs. Also, the extent of diffuse Fe storage in the catchment surface waters is revealed by high flow Fe loads that reach up to 50g/s, several orders of magnitude higher than maximum low flow load of 0.39g/s. Crucially, load values indicate that both coal and oil shale mine areas contribute Fe and SO_4^{2-} to surface waters, confirming the influence of abandoned oil shale mine sites on poor water quality. Major ion chemistry data indicates that in coal mining areas Ca, Mg and SO_4 dominant surface waters due to the input of coal mine waters, while in oil shale mining areas Na and Cl become increasingly dominant. It is suggested this is related to 1) the influence of urbanisation and sewage treatment and 2) the influence of Na-Cl water discharged from unprocessed oil shale waste, consistent with water discharged from shale wastes elsewhere in the UK (e.g Banks et al. 1997). Identification of this Na-Cl signature is also significant to modern day unconventional hydrocarbon exploitation as waters with similar chemical signals have been documented returning to surface

following drilling and hydraulic fracturing in the USA (Haluszczak et al. 2013). Significant scientific challenges remain for unconventional hydrocarbon exploitation in the UK and in particular, what will the composition of flow back waters be from UK shales? This Na-Cl signature suggests similar waters might be expected from oil shale exploration in the UK.

Recommendations are made to improve the surface water monitoring network principally to allow for a more accurate characterisation of mine contamination from oil shale mine regions. This would involve monitoring Fe and SO₄ on a number of catchment tributaries which are currently unmonitored and also ensuring that where Fe is sampled SO₄ is also sampled.

7.2.3 Mine waste

In Chapter 5 a detailed lithological, mineralogical and historical investigation of four mine waste sites representing the range of mine waste types in the Almond catchment is presented. Investigations involved the recovery of mine waste samples at depth, water sampling and analysis, XRD analysis and geochemical modelling. The four sites investigated are: 1. an ironstone mine waste; 2. a coal mine waste where a treatment system has been installed; 3. a second coal mine waste; and 4. a small oil shale mine waste site.

Site 1 is found to have a significant impact on the local surface water quality and potentially on groundwater due to the discharge of low pH waters containing elevated Fe, Mn, Al and SO₄. Fe precipitate formation is observed for over 1km along the discharge stream prior to confluence with the Almond River. Mineralogical investigation and geochemical modelling indicates that this impact is related to minor K-jarosite and pyrite content in the waste which consists predominantly of clay and sheet aluminium silicate minerals. Dissolution of the acid producing jarosite and oxidation of pyrite (up to 5mmol/kg H₂O) due to the availability of oxygen in the waste pile is responsible for high Fe and SO₄²⁻ concentrations (Stumm & Morgan 1981, Backes et al. 1986). Also carbonate mineral availability is limited and buffering of the discharge pH restricted, resulting in low pH (2-4). Consultation with

catchment geology indicates that while the site poses a significant threat to local water quality, ironstone bands are not common compared to other mineral resources in the catchment and the total volume of the waste is likely to be limited. On a national scale these findings are significant because although ironstones are considered to be a subordinate sedimentary facies (Houten & Bhattacharyya 1982) significant exploitation has occurred in some areas of the UK (Palumbo-Roe & Colman, 2010). Younger (2002) documented the environmental impact of subsurface ironstone mining where pyrite content of worked strata and the resulting oxidation posed a significant water quality threat. It is unclear whether the same ironstone and high pyrite content relationship is present at all ironstone mine sites. However the evidence suggests most ironstone sites are of significant environmental concern.

Site 2 discharges waters which are less so contaminated than Site 1 but still contain elevated Fe and SO_4 , ~ 80 and 670mgL^{-1} respectively. The impact on surrounding surface waters is reduced, but not eliminated, by the treatment system operating at the site. Fe precipitate formation is still observed in local surface waters impacted by the mine water discharge which is likely to have implications for river ecology and bio-diversity (Jarvis & Younger 1997). Mineralogical investigation indicates that the waste contains discrete hotspots of slightly elevated jarosite (up to 1.73wt%) and pyrite content (up to 1.49 wt%) surrounded by a waste of clay, sheet aluminium silicates, feldspars, limited carbonate and quartz. Dissolution of jarosite and pyrite in hotspots is the most likely cause of acidic production and Fe and SO_4^{2-} release (Stumm & Morgan 1981, Backes et al. 1986) indicated in the geochemical model solutions. The maintenance of a neutral pH, by carbonates, in the discharge waters is mostly likely due to the limestone trench installed as part of the treatment system and not the general buffering capacity of the waste pile (PIRAMID 2003). Coal seams are common in large sections of the catchment geology and depth of the mine at this site means that the waste could have been mined from any number of lithologies within the Passage Group, Upper Limestone Formation and Limestone Coal Formation. This variable lithology is partly thought to be responsible for the hotspots of acid producing minerals in the waste pile. Evidence also suggests that the settlement pond sediments associated with former pumped mine waters became

enriched in acidic producing minerals. Due to the presence of the mine shaft directly below the minewaste pile, its also likely that the mine waste is having a direct impact on groundwater due to the downward movement of contaminated mine waters.

Site 3 consists of two different lithology mine wastes; one with a sandstone dominant signature while the other contains a mudstone dominant mineralogical signature. Clay and sheet aluminium silicates in a similar arrangement to Site 1 dominate the first lithology, however, no jarosite and pyrite content is identified. Some limited field evidence of oxidation reactions are observed suggesting a very low (<1%) content of pyrite. The second lithology contains quartz and feldspars in higher quantities but also has no jarosite or pyrite content. The result is discharge water with only slightly elevated Fe ($\sim 1\text{mg l}^{-1}$) and low SO_4 ($\sim 21\text{mg l}^{-1}$) resolved by the geochemical model as being due to the slight influence of pyrite oxidation (0.29mmol/kg). It is likely that siderite dissolution maybe of greater influence on the discharge chemistry than the model solution implies (Younger 2004). Limited Fe precipitate formation is observed at the discharge point and downstream impact on water quality is likely to be minimal. This site is complicated by the natural discharge arrangement as waters pass through a small peat bog area, analogous with an anaerobic mine water treatment system (Hedin et al 1994, PIRAMID 2003), prior to discharge. It is possible this reduces concentrations of SO_4 and metals in the discharge via sulphate reduction processes (Hedin et al. 1994).

The difference between the discharge waters at Site 2 (prior to treatment) and Site 3 highlights an import issue associated with coal mine wastes. Any number of lithologies with or without significant pyrite content is termed coal mine wastes. Therefore, classifying potential environment impact associated with a coal mine waste on a regional or catchment scale is troublesome. While preliminary assessment based on the source of the waste rock may give an indication of pyrite content (Spears et al. 1999) accurate predict and understanding of environmental impact requires detailed mineralogical and chemical assessment and modelling (e.g. Evans et al 2003) . Also, XRD analysis should probably be supported by XRF and other analysis particularly when the mineralogy below 1 wt% may influence the leachate

composition. While the results from Site 3 were not conclusive they suggest the possibility of mine waste leachate being controlled in part by siderite and or ankerite dissolution. It is likely both these minerals were of greater influence at Sites 1 and 2 than revealed by the model solutions. Younger (2004) commented on how Fe carbonates are likely to be of significant influence on mine waters. This suggests that preliminary '*modelling for sulphide mineral weathering, and attenuation of acidity by calcite and aluminosilicate weathering reactions*' (Bamwart & Malmstrom 2001) at mine sites is likely to overlook some of the complexity of north west Europe's Westphalian coal measures which are calcite poor and Fe carbonate rich (Younger 2004).

Site 4 differs from the other three sites because the history of the oil shale industry has significantly altered the mineralogy of the majority of waste at the site from a raw oil shale to an orange red processed oil shale waste. The processed waste lacks any identifiable pyrite and contains variable hematite, carbonate, quartz, feldspar, mullite and corderite content. Sampled waters are thought to be only partially influenced by the waste mineralogy and contain elevated Fe (2.4 mg l^{-1}) and Mn (3.29 mg l^{-1}). Geochemical modelling suggests that feldspar, carbonate and also hematite dissolution maybe operating in the waste site but that pyrite oxidation in the black unprocessed oil shale is the most likely source of Fe. The impact of the discharge on water quality is minimal; however, the investigation indicates that larger oil shale mine wastes sites in the catchment may discharge a significant diffuse quantity of Fe to catchment waters.

The investigation at Site 4 indicates that the impact of small individual sites within the Almond is limited, particularly when sites contain only small quantities of unprocessed black, potentially acidic oil shale. The combined impact of the larger sites, if they contain a significant quantity of unprocessed shale may be significant and the surface water quality presented in Chapter 4 suggests Fe and SO_4^{2-} discharge to surface water in oil shale areas is significant. The Estonian example (Puura 1998, Puura 1999, Saether 2004) confirms that oil shale wastes elsewhere discharge similarly contaminated leachates although in Estonian there are issues with very high

pH discharges due to a dominance of carbonate minerals in the oil shale source rocks.

Oil shale mining and exploitation is being proposed and piloted in Australia where the estimated reserve equals 4.8 trillion barrels and a moratorium on mining of oil shale has just been lifted- Feb 2013 (Australian Mines Atlas 2013). The main areas of exploration have been in East Queensland where oil shales are classified as torbanites and contain quartz, clay minerals, siderite, carbonate minerals and pyrite (Dyni 2005). Therefore, depending on the amount and type of processing the proposed oil shale wastes and mines in Australia could produce acidic discharges of environmental concern.

Exploitation and mining operations for oil shale are also known to be on going in China and Brazil with smaller reserves in many other countries (Dyni 2005). In the USA however oil shale exploration and extraction primarily through drilling and hydraulic fracturing has increased rapidly in recent years together with shale gas exploitation (Maugeri 2013). The potential discharge waters associated with this time of exploitation differ in some ways from those associated with oil shale mine wastes (Haluszczak et al. 2013); however, the potential resulting environmental impacts if not managed correctly may be similar if not worse. Hence why the example of historic oil shale exploitation documented in this thesis is still significant today when there is an economic move toward trying to exploit other UK unconventional hydrocarbon reserves (DECC 2011).

7.2.4 Mine water hazards

Chapter 6 documents the results of detailed sampling investigations into the mine water chemistry of mine sites in the Almond catchment. The sampled mine waters are characterised using a number of common chemistry and hazard classification schemes. Mine water hazard is then mapped across the catchment using mine site characterisation, location from the GIS map presented in Chapter 4 and a digital terrain model is designed to identify surface water catchments.

Five mine water sources are considered; Ironstone, Coal and Oil Shale mine waste and flooded coal and oil shale mines. The classification schemes utilised are; the Piper diagram (Freeze and Cherry 1975, Fetter 1994), a simple Fe vs. pH plot, Alkalinity vs. SO_4 dominance (Younger 1995, Rees et al. 2002) and MAMDI hazard classification (Gray 1996, Kuma et al 2011). Sampling and classification revealed that ironstone mine waste discharge low pH (2-4), heavily mineralised waters containing elevated Fe (up to 160mg l^{-1}) and SO_4 (up to 1900mg l^{-1}) due to high pyrite and K-jarosite content, rapid oxidation and dissolution reactions and limited carbonate and silicate buffering. Coal mine waste discharge variable chemistry waters; when pyrite is present waters show neutral pH with elevated Fe (up to 80mg l^{-1}) and SO_4 (up to 1800mg l^{-1}) however much lower concentrations are also recorded at some sites. This is interpreted as being related to the variable nature of coal measure lithologies (Cameron & Stephenson 1985, Browne et al 1999) with many containing limited or no acidic production potential. Accurate characterisation of the range of coal mine waste lithologies and potential hazard is an area highlighted where further research is necessary. Oil Shale mine waste are depleted in pyrite due to the industrial processing of the shales, however, moderately mineralised pH neutral waters containing slightly elevated concentrations of Fe and Mn are discharged. This could be the result of pyrite in unprocessed oil shale (Bailey 1927, Louw & Addison 1985) or possibly the weathering of hematite in the processed oil shale (Faust & Aly 1981). Flooded coal mine waters are generally of neutral pH, contain elevated Fe (up to 50mg l^{-1}) and SO_4 (up to 1500mg l^{-1}) and have high alkalinity. This is interpreted as being due to the influence of pyrite oxidation (Stumm & Morgan 1981) and the high availability of carbonate minerals to buffer pH within the mine prior to discharge at surface (Younger 2004). Flooded oil shale mine waters are moderately to heavily mineralised but contain only slightly elevated Fe, low SO_4 and are alkaline. Abandonment age (Wood et al. 1999), the reduced availability of oxygen and generally lower pyrite content in the Scottish Oil Shale Group are thought to be the principal factors resulting in the much lower contaminant concentrations compared to flooded coal mines.

Mine sites in the catchment were ranked based on the chemical characterisation outlined together with the MAMDI classification (Kuma et al 2011). The catchment was then divided into 40 sub-catchment areas, the number of each mine site type in each area and the sum of mine site ranks was calculated and used to assign an overall mine water hazard rank for each sub-catchment. Four mine water hazard ranks for catchment areas were assigned: A- Limited, where only a small number of mine sites are found with some potential for local water quality impact but limited impact on whole catchment water quality, B- Significant, in areas with clustering of some mine sites with possible interconnected workings and mine wastes with some potentially significant impacts on local water quality and a diffuse influence on wider water quality, C-Important, moderately dense clustering of mine sites with interconnected workings, mine waste and significant impacts on local water quality and diffuse influence on catchment water quality and groundwater, D-Extensive, dense clustering of mine sites with interconnected workings, large mine waste volumes, high impact on local surface water quality and significant diffuse impact on catchment water quality and groundwater.

While the map produced is preliminary and would benefit particularly from more accurate characterisation of coal mine waste hazards, in general it is considered a useful tool for assessing mine water hazard particularly when used with other environmental assessment methods such as groundwater vulnerability maps (O'Dochartaigh et al. 2005). Also, the map should aid future corrective management, decision making; particularly in improving monitoring networks for assessment of diffuse mine water contamination (Johnston et al. 2008). The map highlights a pressing issue associated with the targets for water quality improvement outlined by the EU WFD in a region where no mine water remediation or improvement actions have been proposed.

7.4 Catchment conceptual model

The key sources and processes of contamination in the Almond River Catchment revealed by this study are summarised and conceptualised in Figure 7.1.

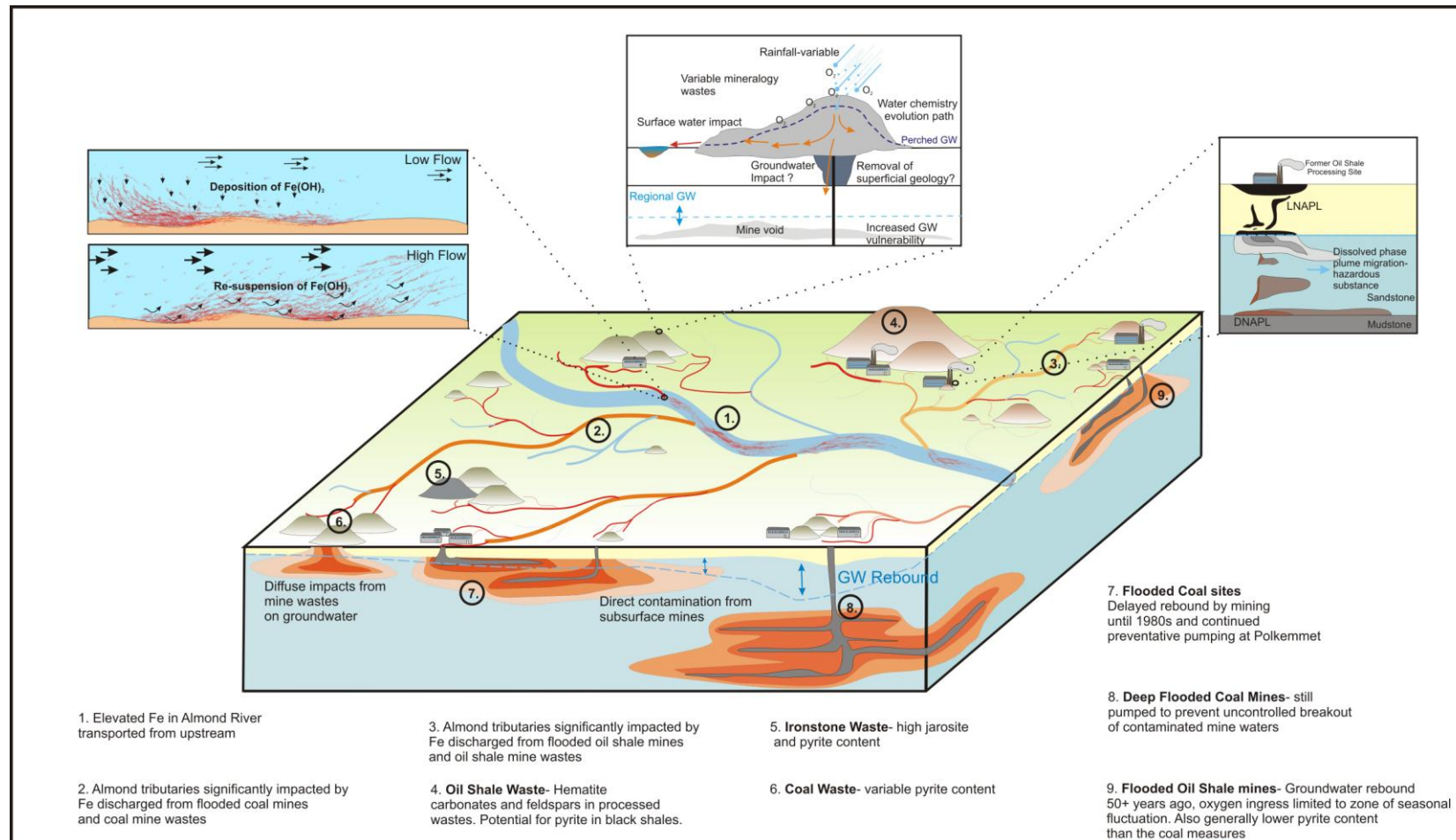


Figure 7.1- The Almond Catchment conceptual model. The diagram indicates the main mine sites present within the catchment and shows the main impacts on groundwater and surface water. A brief description of each of the different sites and impacts is given.

7.5 Further work

This body of research indicates a number of areas where further research would improve the characterisation of hazards within the Almond Catchment and, more generally, in the field of resource exploitation. These are outlined below;

- The work presented here highlights that coal mine wastes can have variable mineralogy and chemistry. At present this variability and its relationship to mine waste lithology is poorly defined. More work is needed to properly ensure the variability in mine waste is understood and managed correctly in Scotland and elsewhere in the world. This is particularly important as mining industries in the modern day are increasingly undertaken in the developing world (World Coal Association 2012) where environmental and natural resource management is often not conceived or applied correctly (Warhurst 1994, Ascher 1999). In the first instance, in Scotland, this would probably take the form of an inventory of closed waste facilities which is already a requirement under the Mining Waste Directive 2008.

‘Article 20 of the Directive requires Member States to ensure that an inventory of closed waste facilities, including abandoned waste facilities, is drawn up, periodically updated and made available to the public by 1 May 2012. The Inventory should include only those sites which cause serious negative environmental impacts or have the potential of becoming in the medium or short term a serious threat to human health or the environment. The Scottish Government is considering how best to take this work forward. Once a national Inventory is complete, it may be appropriate to pass this work on to local authorities so that they can maintain, and update, the Inventory for sites in their areas as required by the Directive.’ Mine Waste Directive Consultation Paper, Planning Scotland, April 2008, Part II Transposing the directive.

Unfortunately, it appears that no such inventory for Scottish mine waste is in the public domain at present. However, the Environment Agency has released an inventory for England and Wales. It is likely that no similar document will be released for Scotland and it is understood, within SEPA, that the responsibility of producing an inventory of closed mine waste facilities will fall to local authorities (Personal communication, Paul Butler SEPA). If an inventory were available one route to improve the characterisation of mine waste would be to select cross section

of sites, in Scotland, to investigate the relationships between mine waste mineralogy, lithology, source rock and water quality impact on a national scale. As the proposal is for the inventories to now be constructed on local authority level this, potentially, increases the need for involvement from a research organisation to ensure consistency of assessment and classification.

- This thesis highlighted the potential for the transportation of trace elements sorbed on to Fe precipitates and their subsequent flow dependent transportation and release to the wider water environment. Detailed investigation looking at the chemical nature of the Fe precipitates in the Almond catchment could indicate the potential extent of this problem. In heavily metal mined areas this problem is likely to be exacerbated. Investigation should focus on the transportation properties of Fe precipitates under variable flow and how this may facilitate the distribution of sorbed trace metals and elements in river catchments.
- Difficulty was experienced in identifying oil shale mine water discharges in the catchment. Since the sampling was undertaken several other discharges have been identified downstream of the Ingliston discharges. Increasing the number of samples would increase confidence in the characterisation of flooded oil shale mine discharges. This could be expanded to areas mined for oil shale outside the Almond Catchment. Also, mine plans were consulted during this research but were not utilised to their full extent. Consultation with, possibly even digitisation of, mine plans is likely to improve the identification of flooded oil shale mine discharges. Increasing the number of oil shale discharge samples, combined with the historic review of the oil shale industry in Chapter 3 would make a useful and informative journal paper publication.
- As stated earlier, the monitoring network in the Almond Catchment has been utilised successfully to demonstrate the input of contamination from both oil shale and coal mining areas. The network, however, needs updating to accurately compare the loading from coal and oil shale mining areas. This would involve sampling at 1. The River Almond prior to confluence with Howburn, 2. Breichwater immediately

following confluence with Longford burn, 3. Broxburn, 4. Niddry Burn, 5. Linhouse Water and 6. Murieston Water. In addition, all those points currently sampled for Fe should also be sampled for SO₄.

- The size of the oil shale wastes in the catchment and a lack of definite discharges at most sites suggests a significant infiltration of water through the waste directly to groundwater, possibly through historic mine shafts and opencast mining areas that the waste has been used to cover. Quantifying this impact based on actual data may be possible via groundwater borehole installations up and down gradient of the sites. Separating the impact of the waste and existing subsurface mines on groundwater chemistry, however, would prove difficult because the subsurface in the area is so heavily mined. Modelling based on the known mineralogy provided in Chapter 3 and 5 or further geochemical experimentation on samples may help to further define this impact. In particular attention needs to be given to the role of black unprocessed shales found at the oil shale wastes sites.
- The mine waste at Whitrigg colliery is known to overlay the historic mine shaft at the site. It is possible that this provides a route for contamination directly to groundwater. As with the oil shale sites the impact of this on groundwater quality would be difficult to assess due to the potentially reduced water quality which already exists in subsurface mines. Calculation of the infiltration rate for the site and comparison with the known discharge around the site from both the treatment facility and other drainage channels could be used to give an indication of the amount of water which moves vertically down to groundwater. Ultimately quantification of this impact would require a detailed subsurface monitoring network and the use of a reactive transport model. This scenario, however, is considered to be relatively common and also analogous with areas where mine waste has been placed on top of naturally occurring pathways for the movement of groundwater. Therefore demonstrating and quantifying the impact may be useful for dealing with groundwater contamination in the Almond but also elsewhere in other heavily mined areas.

- Historic oil shale processing sites and the potential for hydrocarbon ground contamination was identified as a potential risk to groundwater in Chapter 3. Currently no hydrocarbon analysis is undertaken in groundwater and surface water in the Almond. In fact there is effectively no direct sampling of groundwater in the Almond Catchment. This is potentially a high risk area which has been overlooked; particularly as ground contamination from the historic processing site has the potential to discharge hazardous substances to groundwater. Both the Groundwater Daughter Directive and the Water Framework Directive state that the discharge of hazardous substances to groundwater is not permitted.
- The move towards unconventional hydrocarbon exploitation, by various means, in the UK and elsewhere in the world has the potential to result in similar impacts to the water environment as historic mining. These potential impacts are just starting to be quantified in the USA. One of the main issues is with abandonment and long term integrity of exploration and exploitation wells. Looking at the integrity of cements and casings used for exploration and exploitation via laboratory experiments and models could be used to help quantify the long term integrity of well materials. A more representative method might be to study newly abandoned areas in the USA for signs of contaminant migration between aquifer units. This could inform more robust well construction and abandonment methods for more modern in situ unconventional hydrocarbon exploitation. This would of course require cooperation from industry to provide information on the well materials used and abandonment methods employed.
- The UK presents a different environment for the in situ exploitation of unconventional hydrocarbons than that of the USA. Principally because many of the areas where drilling and hydraulic fracturing may be undertaken have already been mined. The potential interaction between fracture propagation and historic anthropogenic preferential pathways in the form of mined ground is not currently well understood. For example, coal bed methane is currently being undertaken near Falkirk in Scotland, how fracture foams and methane will migrate in the ground and possibly into existing mine networks is not well understood. This could be modelled using a 3D groundwater and multiphase flow model but would require accurate

understanding of the subsurface geological arrangement as well as the pressure gradients involved. It is possible that shales and oil shales within mined areas elsewhere in the UK could be targeted such as those in the UK Coal Measures and the Jurassic Lias (DECC2011). Ensuring liquid hydrocarbons do not migrate into overlying aquifers via existing mines is considered to be extremely important. At present the maximum recorded fracture propagation from hydraulic fracturing is approximately 500m. Again a subsurface flow model could be constructed to understand the potential consequences of fracture propagation entering a mined area or natural fracture zone. Would contaminants from process waters or fracture fluids be able to move through existing fracture zones? If so at what speed and when might these been seen at surface, if at all?

- Geothermal energy exploitation from historic mined areas, including oil shale mined areas, in the central belt of Scotland has been proposed in recent years (e.g. Campbell 2010). At present the subsurface arrangement of mines is poorly constrained and this arrangement is likely to be important in maximising heat transfer. Studying historic mine plans and constructing computer representations of the subsurface arrangement can be used in computer models to predict the availability of heat transfer (e.g. Ferket 2011, Streb & Weiber 2011).

7.6 Concluding remarks

This thesis has shown that mine water from different mine industries and mine site types represent a range of potential hazards to the water environment and that the cumulative impact of mining causes poor water quality in surface water and groundwater long after abandonment. The first assessment of the range of potential water quality issues associated with the oil shale industry is presented and a clear link to historic understanding of the industry is demonstrated. Areas requiring improvements in mine water monitoring networks are highlighted and the first catchment scale mine water hazard map is presented. At present there are significant obstacles to overcome if improvements in water quality, as required by legislation, are to be achieved in heavily mined areas. This research represents only one of many steps which need to be taken to apply scientific knowledge and prioritise environmental improvements associated with the legacy of historic mining industries in the UK and elsewhere in the world.

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